FROM MINE TO MICROSCOPE

Advances in the Study of Ancient Technology

edited by

Andrew J. Shortland, Ian C. Freestone and Thilo Rehren

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Contents

Introduction

Michael Tite came to archaeology through a formal education in the sciences, graduating from Oxford with a BSc in Physics in 1960. An interest in archaeology led him on to a DPhil supervised by Martin Aitken, at the Research Laboratory for Archaeology and the History of Art, which had been established some five years. His thesis awarded in 1965 was on the thermoluminescence dating of ceramics, but apparently not satisfied with a single PhD topic, he also worked with Martin Aitken on proton magnetometry and they published several papers on archaeomagnetic surveying at this time. He went on to undertake post-doctoral work at the University of Leeds as an ICI research fellow, and following this was appointed lecturer in the Physics Department of the University of Essex. He continued his work on electromagnetic prospecting and the magnetic susceptibility of soils and it was in this period that, with his PhD student, Yannis Maniatis, he developed his interest in the use of the scanning electron microscope to investigate early ceramic technology, an area in which he is still active. It was while he was in Essex that Mike produced his seminal book *Methods of Physical Examination in Archaeology* (Seminar Press, 1972). This book was the key textbook in the field for over a decade, and it is probably fair to say that no other single author has produced a textbook covering such a wide range of archaeological science – dating, prospection and materials analysis.

Mike's abilities and grasp of the field, as evidenced by his book, made him a clear choice as Keeper of the British Museum Research Laboratory, a post he held from 1975 to 1989. It was during this period that his organisational flair came to the fore. He transformed a rather loose and dilettante group of individuals into what has been described as the world's leading group in the study of ancient technology. His pragmatic approach to individuals' strengths and weaknesses (to paraphrase: "you can't change people's characters, so make the most of them") allowed him to build extremely effective teams to address specific problems, resulting in numerous multi-authored publications. While many of these do not carry his name, he was involved in the direction of virtually every project and read and edited the vast majority, if not all, of the papers produced in this very fruitful period. He strengthened the Department of Scientific Research, as it became known, in many key areas such as statistics, mineralogy, neutron activation analysis and computing; indeed, the department under Mike was largely responsible for the launch of the British Museum into the world of information technology and on-line cataloguing. Mike's deft handling of the issues around an unacceptable error detected in a series of BM radiocarbon dates, and his coordination of the dating of the Shroud of Turin, are just two of his more public contributions from this period. During his time at the BM, London hosted a very successful Symposium for Archaeometry, and Mike joined the Standing Committee for the International Symposium for Archaeometry, serving as Chair from 1988 to 2004. The BM added the duties of Keeper of Conservation to his brief between 1981–5, but he found this brought more problems and less fun, and was able to divest himself of this after a relatively short period, finding the motivations of conservators a good deal more difficult to fathom than those of scientists.

In 1989, Mike Tite left the BM to become Edward Hall Professor of Archaeological Science at the Research Laboratory for Archaeology and the History of Art, Oxford, following in the footsteps of Martin Aitken, his DPhil supervisor. He took over as editor of the journal *Archaeometry*, and expanded

it from a twice yearly cycle to quarterly publication. Mike's period at Oxford saw the development and expansion of the facilities and staff involved in materials analysis, AMS radiocarbon dating, the development of the OxCal calibration program, and the introduction of paleodietary studies and stable isotope analysis. For a time, RLAHA took responsibility for the Isotrace Laboratory, involved in the lead isotope analysis and provenancing of early metals. Many of these activities required a diplomatic touch: as will be clear from papers in the present volume, the spinoff from the great debates over the validity of the lead isotope approach continues, while it was necessary for the Lab to divest itself of its highly successful thermoluminesence authenticity service, due to concerns surrounding the ethics of authenticating material of unknown provenance. Meanwhile Mike continued his interest in early ceramics, and firmly established himself as the leading investigator in the field of early ceramic technology. He supervised a number of outstanding DPhil theses, and a number of his research students have gone on to become leading specialists themselves. His students recall his great ability to remember exactly what was said (and promised) meeting to meeting, which ensured that nothing was "forgotten" or a flaw in an argument ignored. Due to his long experience in ancient materials by the time he was at Oxford, Mike had also developed an almost supernatural ability to "see" solutions and ways forward, which his students learnt to trust and when tested almost always proved correct. Most of all, he is remembered as a supervisor who really cared for his students, their studies and their future careers. He remains an important mentor and friend to many of them.

During his distinguished career, Michael Tite has held four of the most important positions in archaeological science: Director of the labs at the BM and at Oxford, plus Editor of *Archaeometry* and Chair of the International Standing Committee. Thus not only has he led through the strength of his research and publications, but through his administrative and political activities. Those of us who have been privileged to work with him are only too aware that he saw his role as minimising the administrative burden on the rest of us, while undertaking as little admin as possible himself; his focus was always on getting as much science done as possible with the available resources.

As we write, Mike just completed an important book on Egyptian faience, and his output over recent years, evidenced in the accompanying list of publications, has shown no evidence of being diminished by his retirement in 2004. This volume represents a series of contributions by students, colleagues and friends in appreciation of the influence he has had on them, both as a researcher and as a friend. While these contributions cannot be compared with the best of Mike's output, in one way at least we hope they reflect his approach – an overwhelming desire to get to the bottom of a problem.

The editors, 2008

An Apology

This festschrift for one of the great scholars of archaeometry was conceived more than five years ago, and a first preprint was handed to Mike Tite during his retirement party at the Research Lab for Archaeology and the History of Art in 2004. The swiftness and quality with which the authors had produced their papers is testament to the admiration in which we all hold Mike.

Unfortunately, the speed of our editorial performance did not match the initial momentum, and it took us more than four years to make the progress from a single copy to a published book. For this delay we have to apologise: to the authors, who had to put up with repeated requests for proof reading and the vagaries of changing publishers; but most of all to Mike as the recipient of this book. If there is one good thing to come from this delay, then it must be that we were able to include even more papers and books in Mike's still growing bibliography.

We very much regret that it took us so long to bring this volume to completion, and are grateful for everybody's patience in the process.

Andrew J. Shortland, Ian C. Freestone, Thilo Rehren

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Chapter 1

Lead frits in Islamic and Hispano-Moresque glazed productions

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Abstract

The frits and related materials found in an Islamic workshop, San Nicolás (Murcia, 10th century AD), and an Hispano-Moresque workshop, Paterna (Valencia, 13th century AD), are studied. Frits found in Paterna correspond to the production of tin glazes, the use of frits in the lead glazes being discarded. Frits found in Murcia correspond to the production of transparent lead and "cuerda seca" glazes, although frits were used also in the production of tin glazes. A comparison between the archaeological findings and the documentation concerning the raw materials used, the frits and manufacturing processes, as well as differences and similarities in the production techniques between both workshops, is presented.

Introduction

The term "frit" refers to the part of a glaze recipe that has been fired and reground prior to its inclusion in the glaze slip (the homogeneous mixture of glaze materials and water which is applied to the ware by dipping, spraying or brushing). The frit is often an eutectic mixture and therefore fusion begins earlier during the firing and is more thorough, allowing to lengthen the maturing range if required. Frits are used in glazes but also as fluxes in ceramic bodies, slips and engobes (Hammer and Hammer 1997). There exist two types of glazes widely used in ceramic technology since antiquity, alkaline based and lead based, although mixed alkaline/lead glazes are also widely used. The large amounts of gases produced by the decomposition of sodium, calcium and potassium salts seems to be the main reason for the use of alkaline frits. Although lead frits were not widespread used until the first half of the 20th century AD to combat lead poisoning, ancient documents as Abu'l Qasim's "Treatise on Ceramics" (Allan 1973) indicate that lead frits were used at least since medieval times. Nowadays, the main advantage of using lead frits rather than raw lead compounds and silica is to handle less toxic materials, that during firing release fewer toxic volatiles. However, the frit ensures a more uniform distribution of materials, and hence, a more uniform fusion (Hamer and Hamer 1997), and this seems to have been the main reason for their use in antiquity.

The origin of frits seems to be linked to the origin of glass. The use of alkaline frits to glue sand and produce a compacted body is documented in the production of Egyptian faience (Tite et al. 1983). Although lead glazes applied on ceramic pastes were widely used in Roman times, there is neither archaeological evidence nor literature demonstrating the use of lead frits in Roman times. From early Islamic times frits were used in the production of glazes applied over stonepastes and also ceramic pastes (Mason and Tite 1994). The Islamic glazes found are pure alkaline, mixed alkaline/lead glazes and high lead glazes. The introduction of tin in the glazes, producing an opaque white glaze, was also performed in early Islamic times to enhance the coloured decorations (Mason et al., 1997). Ancient texts (Abu'l Qasim's "Treatise on ceramics", Allan 1973) indicate the use of frits in the production of tin glazes.

A lead frit contains fused lead oxide and silica. The amount of lead oxide in a lead frit may vary from 10% to 90%, but the most standard frit is lead bisilicate ($PbO.2SiO_2$) with theoretical weights of 65% PbO and 35% SiO_2, very close to the eutectic composition (70 wt% PbO and 30 wt% SiO_2). Fusion

Table 1: Chemical analyses of lead and tin glazes from the 13th century AD workshops of Paterna. Analyses by microprobe except SnO_2, which was obtained by XRF of scratched powder. Data in wt%, standard deviation in brackets.

	Colour or decorations	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe2O3	PbO	SnO_2	MnO	CuO
lead glazes	green	0.25 (0.60)	0.49 (0.11)	5.25 (0.61)	32.76 (1.53)	0.93 (0.37)	2.59 (0.51)	0.40 (0.04)	2.53 (0.50)	54.62 (11.7)	0	0	0
	yellow	0.10 (0.03)	0.43 (0.13)	5.44 (0.26)	30.28 (1.16)	0.86 (0.23)	2.41 (0.22)	0.41 (0.06)	1.94 (0.19)	57.68 (12.5)	0	0	0
	brown	0.10 (0.05)	0.70 (0.12)	5.49 (0.58)	33.59 (1.09)	0.84 (0.29)	1.44 (0.63)	0.32 (0.03)	2.56 (0.50)	53.11 (5.61)	0	0	0
tin glazes	white	1.03 (0.09)	0.21 (0.05)	2.89 (0.74)	42.28 (1.71)	2.60 (1.43)	1.66 (0.33)	0.07 (0.06)	0.45 (0.32)	41.14 (2.45)	7.72 (0.31)	0.01 (0.02)	0.03 (0.04)
	green and brown decorations	0.53 (0.26)	0.38 (0.15)	3.51 (0.67)	43.85 (2.11)	2.32 (0.76)	2.15 (0.92)	0.13 (0.06)	0.44 (0.15)	38.90 (3.72)	6.55 (0.40)	1.18 (1.61)	0.51 (0.06)
	turquoise green	0.58 (0.22)	0.36 (0.13)	3.43 (0.07)	39.14 (1.01)	2.04 (0.51	1.97 (0.07)	0.06 (0.08)	0.43 (0.07)	44.04 (1.34)	6.56 (1.83)	0.03 (0.02)	2.52 (0.19)
	blue and lustre decorations	0.60 (0.28)	0.43 (0.08)	2.33 (0.10)	45.21 (1.23)	4.62 (0.06)	1.65 (0.09)	0.04 (0.02)	0.22 (0.16)	35.74 (0.50)	9.17 (0.08)	0.02 (0.01)	0.04 (0.01)
	blue decorations	0.53 (0.34)	0.36 (0.12)	2.29 (0.23)	40.33 (1.55)	3.69 (1.82)	1.70 (0.05)	0.02 (0.03)	0.24 (0.12)	42.25 (0.97)	8.63 (0.05)	0.01 (0.01)	0.06 (0.05)

begins approximately at 714°C and is complete by 950°C. This long range of maturation is important and gives its versatility to the bisilicate.

Silica is obtained from natural sands or pebbles (quartz); potassium, sodium and calcium may be obtained from plant ashes, feldspars and calcareous rocks and salts (carbonates, chlorides, sulphates). Lead was obtained from its ore, galena (PbS), which is found in mines. Roasting galena in air it becomes PbO, a process well known since very ancient times as it is part of the metallurgy of lead. Tin is also incorporated in its oxide form cassiterite (SnO_2) and its origin is also linked to the metallurgy.

In this paper we study the archaeological remains of frits and the lead and tin glazes found in two workshops, one Islamic, San Nicolás (Murcia, 10th c. AD), and the other Hispano-Moresque, Paterna (Valencia, 13th c. AD). A comparison between the archaeological findings and the available documentation concerning the raw materials used, the frits and manufacturing processes, as well as differences and similarities in the production techniques between both workshops are presented.

Materials and methods

The materials analysed are the transparent lead glazes, the tin opaque glazes and the remains of frits found in both workshops. The lead and tin glazes were studied and analysed by means of Scanning Electron Microscopy (SEM) and Microprobe (Cameca, SX-50) at 15 kV and 20 nA probe current over a polished cross section of the glazes.

Chemical and mineralogical analysis of the frits and related materials were performed by X-ray Fluorescence (XRF) and conventional X-ray Diffraction (XRD) on powdered material. A set of PbO-SiO_2-SnO_2 patterns was specially made to obtain good reference XRF data.

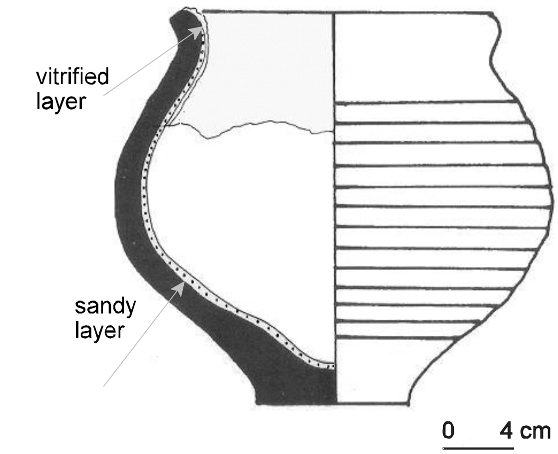
Thin sections of selected frits were analysed by means of Optical Microscopy, SEM-EDS and Synchrotron Radiation-XRD (beamline 9.6 at SRS-Daresbury, UK, 0.867 Å wavelength and 200 microns spot size).

Results

First a summary of the main characteristics of both workshops, previous studies of the ceramic productions and, in particular, of the lead and tin glazes is given. Then, the results obtained from the analysis of the frits, lead glazes, and tin glazes studied in each workshop will be presented.

The Hispano-Moresque workshop from Paterna

Paterna is a town placed close to Valencia, known by its long tradition in pottery production, especially important in medieval times (13th to the 16th centuries AD). The Hispano-Moresque Paterna pottery is well known because of its wide distribution all over the Mediterranean area and also because of its high technological achievement. After the Conquest of Valencia by the Catalan king Jaume I (1238), the Muslim potters remained under the protection of the Christian lords and continued the pottery production (Mesquida 2001). Ceramic workshops were con-



(Design after Mesquida 1989)

Figure 1: Crucibles from the 13th century AD workshops from Paterna showing the protective sandy layer and the vitrified layer.

tiguous to each other and produced large quantity of table and house ware. Ancient documents refer to "Olleries Majors" (Major Potteries) and "Olleries Xiques" (Minor Potteries). Mesquida (1987, 1989, 1990, 2001) excavated extensively the Major Potteries finding three different workshops dated to the end of the 13th century where all kind of house pottery was produced: biscuit fired big jars for containing water, wine or oil, and glazed jars and table ware with either a transparent lead glaze or a white tin glaze decorated in green and brown or blue and lustre (the most precious production). The ceramic production and raw clay materials found in the workshops were extensively analysed (Molera et al. 1996). Analyses of the glazes (Molera et al. 1997) indicate that the transparent glazes are high lead glazes that showed a honey or green colour due to the presence of Fe^{3+} and Fe^{2+} respectively. White glazes correspond to opaque lead glazes due to the addition of 6–9% of SnO_2 (Vendrell et al. 2000; Molera et al. 2001a). The tin glazes related to the lustre production are potassium richer (Molera et al. 2001b), and this fact is linked to the manufacture of lustre (Pradell et al. 2004). A summary of the chemical compositions of the different glazes is given in Table 1.

Concerning the frits, large amounts of cooking pot fragments with remains of the frits were found (see Fig. 1). Consequently, these cooking pots were identified as crucibles for producing frits (Mesquida 2001). These crucibles have a flat base and globular thick walls covered inside with a white sandy layer, and some present remains of a second vitreous layer attached to the sandy layer in the upper inner part close to the neck. The presence of this vitrified layer at the top of the crucibles seems to indicate that they were fired in the kiln. Most of the fragments present also external drops and trickles. A full description and chemical and XRD analysis of the sandy layer, vitrified inner layer and outside drops and trickles are given in Table 2.

The sandy layer contains large amounts of quartz and potassium feldspars, sanidine and orthoclase, and minor proportions of calcite. Calcite is a contamination phase resulting from burial and weathering. Quartz and feldspars are then the principal compounds. The grain size distribution of the sandy layer was measured by laser granulometry (Coulter LS) giving an average size of 130 microns (ranging from 50 to 250 microns).

The chemical composition of the vitreous layer is very heterogeneous, containing quartz and potassium feldspars as main compounds. Moreover, lead feldspars, lead silicates and some cassiterite (SnO_2) are also found, and their presence is due to the reaction between the frit and the sandy layer. The colour of this vitreous layer is mainly white or grey, but a few are green. The presence of a sandy layer covering the inner walls is described in other workshops (Coll and Camps 1994) and has been identified as a protection to avoid that the frits stick in the crucibles. The crucibles appear all broken *in situ*, indicating that they were broken after cooling to extract the solidified frit.

Finally, the outside drops and trickles have a chemical composition and colour characteristic of a tin glaze frit. The main compounds are cassiterite (SnO_2), quartz and a vitreous phase. In minor amounts they contain lead feldspars and lead silicates, and a few of them contain cristobalite. The presence of cristobalite indicates that a temperature of at least 1025°C was reached during the production (Hlavác 1983). We will consider that these drops have the final frit composition used in the production of the tin glazed pottery. The frit was made mixing PbO, SnO_2 and sand. Subtracting the amount of PbO and SnO_2 we obtain the composition of the sand used in the production of the frit, which is also given in Table 2. From this composition we could calculate that this sand contained 75% of quartz and 25% of feldspar – $(K_{0.6}Na_{0.4})AlSi_3O_8$.

All the frits and related materials found in the workshop correspond to the production of tin glazes. There is no evidence of the use of frits in the production of the lead glazes. How these frits were used and applied to produce the tin glazes and how the lead glazes were produced will be discussed in the next section.

Table 2: Chemical analyses of the sandy layer and drops from the 13th century AD workshops of Paterna. Analyses by XRF of frit patterns. Data in wt%, standard deviation in brackets.

	Description	Chemical analysis									Mineralogy	
		MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	PbO	SnO_2	Major	Minor
sandy layer	whitish	0.25 (0.14)	9.96 (2.79)	68.81 (5.01)	2.72 (0.34)	1.31 (0.35)	0.35 (0.15	0.35 (0.11)	14.99 (3.18)	0.70 (0.88)	quartz, K- feldspars : *orthoclase, sanidine*	calcite
Inner vitrified layer	white to grey	0.42 (0.06)	7.18 (3.53)	52.04 (2.97)	1.84 (0.20)	1.35 (0.36)	0.15 (0.10)	0.30 (0.12)	33.84 (2.42)	2.11 (1.15)	quartz, K-feldspars : *orthoclase, sanidine*	lead feldspars : $PbAl_2Si_2O_8$ lead silicates : Pb_2SiO_4 cassiterite
Outside drops and trickles	white	0.11 (0.02)	1.94 (0.10)	37.90 (0.78)	1.01 (0.03)	0.49 (0.07)	0.02 (0.01)	0.19 (0.02)	50.16 (1.06)	7.64 (0.10)	vitreous phase cassiterite quartz	cristobalite lead feldspars : $PbAl_2Si_2O_8$ lead silicates : Pb_2SiO_4 $PbSiO_3$
Sand from the frit		0.26	4.63	90.48	2.41	1.17	0.05	0.45	-	-	75 wt% quartz 25 wt% feldspar : $K_{0.6}Na_{0.4}AlSi_3O_8$	

The Islamic workshop of San Nicolás (Murcia)

Navarro Palazón (1990) documented the archaeological findings of an islamic workshop placed out-walls of the medieval Islamic *Madîna* of Murcia which was dated to the beginning of the 10th century AD. The main ceramic production is of open forms, "ataifores" (bowls) and "jofainas" (basins), most of them biscuit fired and only a few of them glazed. In most of the cases the pieces show important firing defects (firing wastes). The closed forms are very similar to the Madina't al-Zahra and Ilvira productions (Navarro Palazón 1990) namely jars, "orzas" (a kind of cooking pot), cauldrons and candleholders, all of them glazed. A summary of the types of glazes found as well as the chemical analysis are given in Table 3. The materials include brown and green decorated tin glazes, partial "cuerda seca" glazes, yellow transparent lead glazes decorated in brown or green and green and brown transparent lead glazes.

The excavations provided unfired pots, bars to hold the ceramics in the kiln called "atifles", fragments of cauldrons with sticking fused frits, and the most interesting finding, a set of 12 "orzas" containing remains of frits (see Fig. *2)*.

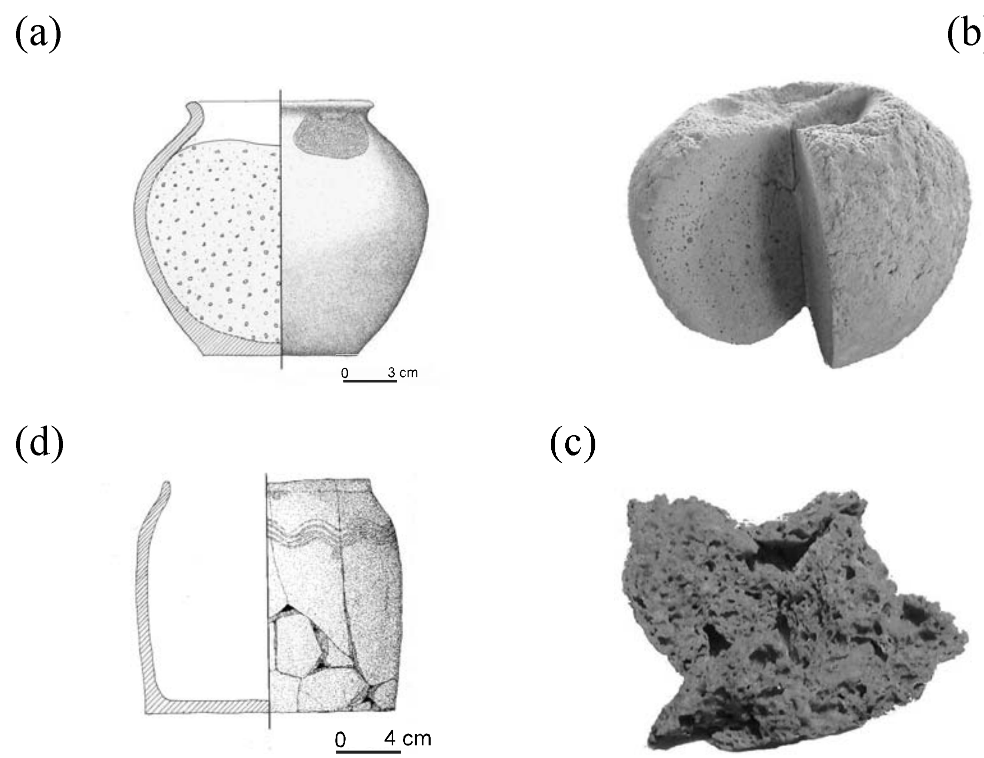
The material found inside the "orzas" has a rock consistence and a ball morphology (diameter of about 20 cm). Large amounts of fragments belonging to these kind of "orzas" appear broken *in situ*, and it is also known that these "orzas" were not for sale. Archaeologists think that the frit was fired in these containers and, after cooling, the "orzas" were broken to extract the frit (Navarro Palazón 1990). Small pieces from the consolidated material of seven different "orzas" and a full frit ball were analysed. For the balls SF01 to SF07 we could only obtain material from the surface while for the ball SF13 we could analyse the whole section of the ball. Figure 2 shows a photography of the full frit ball and of a fragment of one of the frits extracted showing some vitrification.

An important amount of fragments of cauldrons made with a coarse paste showing thick glassy drops and trickles on the surface were also found (see Fig. 2). The frit remains were also studied and analysed. Archaeologists consider that these cauldrons were used to melt the frits that were poured as a viscous liquid at high temperature. The presence of superimposed drops seems to indicate that the cauldrons were reused several times. The inner walls of the cauldrons present a layer of a white to pale pink powder showing different degrees of consistence (from disaggregated to consolidated) that was also analysed. Finally, a fragment of a fully vitrified yellow inform glass (4 centimetre size) was also found and analysed. A full description of the materials analysed and the chemical and XRD diffraction data obtained is given in Table 4.

All the ball frits have similar chemical composition except the ball SF13 which is PbO richer. Moreover, the ball frit fragments show different degrees of vitrification while the ball SF13 (Fig. 2b) does not show any vitreous phase. The ball SF13 is formed by quartz and PbO grains (litharge and massicot) stuck together by a cement made mainly of cerussite ($PbCO_3$) and traces of calcium-lead silicates, lead silicates and anglesite ($PbSO_4$). In contrast, the other

Table 3: Chemical analyses of lead and tin glazes from the 10th century AD workshops of St Nicolas. Analyses by microprobe except SnO_2, which was obtained by XRF of scratched powder. All analyses are the average of at least 20 microprobe points. The tin glazes are analyses of the glass with the cassiterite particles calculated by image analysis at 7–10% in all cases. Data in wt%, standard deviation in brackets.

	Colour or decorations	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	PbO	SnO_2	MnO	CuO
lead glazes	green	0.82 (0.11)	0.35 (0.08)	2.75 (0.48)	35.34 (0.14)	2.78 (0.54)	2.98 (0.19)	0.10 (0.01)	3.70 (2.08)	49.65 (0.36)	0	0.01 (0.01)	0.02 (0.01)
	yellow	0..82 (0.11)	0.39 (0.17)	2.91 (0.52)	34.22 (1.13)	1.78 (0.24)	3.20 (0.34)	0.17 (0.24)	1.43 (0.66)	54.23 (1.52)	0	0.04 (0.04)	0.04 (0.06)
	brown	0.52 (0.04)	0.38 (0.01)	3.31 (0.50)	32.54 (0.27)	1.63 (0.48)	3.50 (0.63)	0.11 (0.02)	1.71 (0.50)	53.01 (2.30)	0	0.39 (0.24)	0.02 (0.04)
tin glazes	white	1.61 (0.17)	0.33 (0.20)	0.71 (0.82)	38.11 (2.42)	1.62 (0.19)	2.17 (0.62)	0.03 (0.04)	0.53 (0.39)	52.03 (4.57)	2.02 (0.59)	0.04 (0.05)	0.02 (0.03)
	green and brown decorations	1.01 (0.26)	0.18 (0.12)	0.55 (0.45)	33.50 (3.47)	1.35 (0.40)	1.29 (0.60)	0.01 (0.02)	0.33 (0.19)	58.55 (5.23)	2.68 (2.18)	0.29 (0.56)	0.03 (0.03)



(Design after Navarro Palazon 1990)

Figure 2 (a): Drawing corresponding to an "orza" containing a ball frit, (b) photography of the consolidated raw ball frit, (c) photography of a fragment of a fired ball frit and (d) drawing of the cauldrons all them found in the 10th century AD workshop from San Nicolás.

ball samples did not contain PbO grains but a vitreous phase, calcium-lead silicates, lead silicates and cerussite. We consider that the ball SF13 was not fired and therefore it contains the consolidated raw frit while the rest of the balls were already fired and contain the frited material.

The raw frit ball contains quartz and red-brownish and yellow lead rich grains. Micro-XRD of the red-

Table 4: Chemical analyses of the frits and related materials from the 10th century AD workshops of St Nicolas. Analyses by XRF of frit patterns. Data in wt%.

	Description		Chemical analysis										Mineralogy	
			MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O3	PbO	SnO_2	CuO	Major	Minor
Ball frits	SF01	fired	0.39	1.85	35.84	0.11	3.89	0.02	0.33	56.61	0	0	vitreous phase quartz cerussite : $PbCO_3$	Calcium-lead silicates : $CaPb_8(Si_2O_7)_3$ $Ca_2Pb_3Si3O_{11}$ Ganomelite : $Pb_9Ca_6(Si_2O_7)_3(SiO_4)_3$ lead silicates : $Pb_3Si_2O_7$
	SF02		0.27	1.18	35.04	0.07	4.18	0.06	0.29	58.01	0	0		
	SF03		0.83	2.57	38.52	0.21	5.34	0.10	0.54	50.95	0	0		
	SF04		0.48	1.28	40.07	0.12	3.89	0.07	0.36	52.60	0	0		
	SF05		0.50	1.46	37.73	0.10	3.96	0.06	0.35	54.66	0	0		
	SF06		0.35	2.40	37.80	0.10	4.35	0.07	0.39	53.28	0	0		
	SF07		0.65	1.48	38.67	0.15	3.93	0.12	0.34	53.73	0	0		
	SF13	raw	0.57	1.43	30.99	0.20	4.23	0.01	0.22	61.98	0	0	quartz litharge, massicot cerussite : $PbCO_3$ hidrocerussite : $PbCO_3{\cdot}2(OH)_2$	Ganomelite : $Pb_9Ca_6(Si_2O_7)_3(SiO_4)_3$ Calcium-lead silicate: $CaPb_8(Si_2O_7)_3$ anglesite : $PbSO_4$
glass	SF12	yellow	0.33	4	32.71	1.12	2.38	0.18	0.99	57.63	0	0	vitreous phase	
drops	SF111	vitreous	0	0.31	37.45	0.19	1.31	0.15	0.48	58.63	0.33	1.29	vitreous phase quartz	calcite, gehlenite anglesite :$PbSO_4$
	SF112	vitreous	0	0.29	35.84	1.15	0.53	0.09	0.60	60.24	0.25	1.13		
protect ive layer	SF110	pink powder	0.67	5.52	73.59	0.24	10.9 3	0.89	2.68	4.26	0	0	quartz	calcite, gehlenite

brownish grains indicates that they are mainly made of PbO (litharge and massicot) and contain small crystallites of lead silicates. The yellow grains contain cerussite, hydrocerussite, lead sulfates and ganomelite (calcium-lead silicate). Therefore, we conclude that the yellow grains are the same as the red-brownish grains but more weathered. From these analyses it appears that the PbO grains were the results of a previous roasting process of the lead ore (galena).

The fired frit ball fragments contain a yellow green glassy material with a high density of bubbles (Fig. 2c). It indicates that these frits were fired inside the "orzas" in the kiln and can explain the lower PbO content of these frits compared to the raw ball frit.

The remains of an inner protective layer and drops and trickles in the cauldrons suggest that they were used somehow in the production of the lead frits. The inner protective layers are very thin and made of sand (quartz and calcite) like in Paterna. The drops and trickles analysed are mainly vitreous containing bubbles (filled with anglesite, an alteration phase) and large amounts of quartz grains, some calcite and gehlenite. They have copper as colouring, indicating that these frits were used for the production of the "cuerda seca" decorated ceramics.

Finally, the fragment of yellow glass appears fully vitrified and has the same composition as the lead transparent glasses found in the workshop.

All the frits and related materials found in the workshop correspond to the production of transparent lead and "cuerda seca" glazes and none of them is related to the production of tin glazes.

Discussion

In this section we will discuss the technology of manufacture of the lead and tin glazes produced in both workshops, that is, how the frits were applied over the ceramic paste, directly or mixed with other materials; which raw mixtures were used in the ceramic productions for which frits are not found and the use of single or double firing in the production of the glazed pottery. A comparison between the frits and glaze production technology as well as between both workshops is also given.

The Hispano-Moresque workshop from Paterna

Transparent lead glaze frits are not found in the workshop. The lack of biscuit fired ceramics for the lead glazed productions and the thick ceramic/glaze

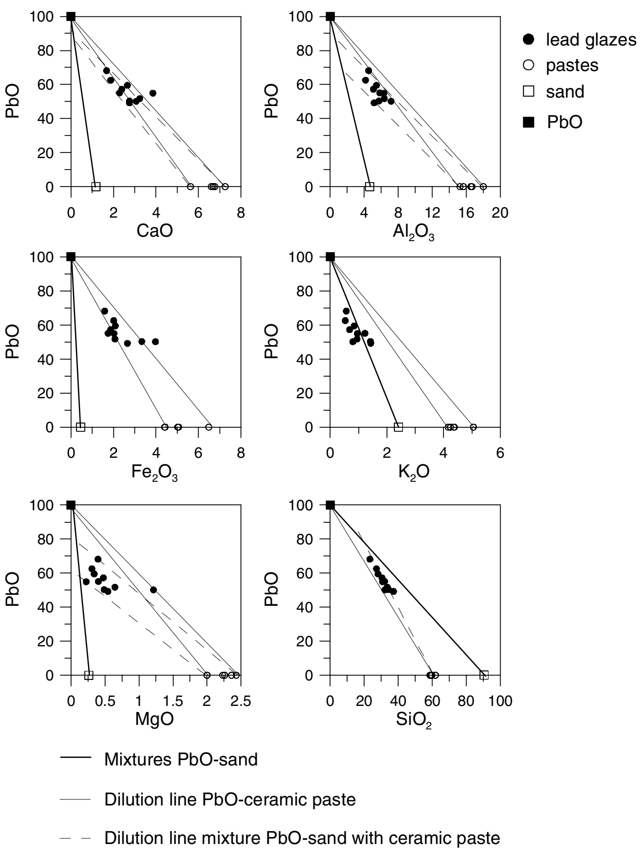


Figure 3: Binary chemical plots corresponding to the transparent lead glazes, ceramic pastes, PbO and sand corresponding to the 13th century AD workshops from Paterna. The possible mixtures of PbO and sand are marked in a thick solid line, the dilution of ceramic paste into the PbO with a thin solid line and the dilution line of ceramic paste into a mixture of PbO and sand with a thin dashed line.

interfaces found in these productions (Molera et al. 2001c) strongly suggest that the lead glazes were obtained by direct application of a raw mixture containing PbO on the ceramic. In this case it is also interesting to determine if the PbO was directly applied over the ceramic or if it was mixed with clay, sand or other materials previous to its application. In order to assess this, binary chemical plots of the lead glazes and the corresponding ceramic pastes over which the glazes were applied are shown in Figure 3. Some extra dots corresponding to pure PbO and to the sand given in Table 2, and a thick solid line corresponding to all the possible mixtures between PbO and the sand are also drawn. Finally, thin solid lines corresponding to the dilution of some ceramic paste in the PbO, and thin dashed lines corresponding to the dilution of some ceramic paste in a mixture of PbO plus sand are also plotted. The plots corresponding to SiO_2 versus MgO, Al_2O_3 and CaO seem to indicate the use of a mixture of PbO and sand (about 15–30 % sand), while the higher relative amounts of Fe_2O_3 and lower relative amounts of K_2O are not consistent with that interpretation. However, on the one hand we must consider that the colour of the glazes is due to the presence of iron, and thus it is expected that some iron was added in order to enhance the colour. And, on the other hand, the relative low K_2O content of the glaze must be attributed to the formation of important amounts of mixed lead-potassium feldspars in the reaction layer that retain most of the potassium diffused from the paste into the glaze (Molera et al. 2001c). Although it is also possible that some clay was mixed with the raw glaze mixture to facilitate the application, this will be hardly obtained from chemical data as the chemical composition of the clay is the same as that of the ceramic pastes.

From these results we can thus accept that a mixture of PbO, sand and ochre was applied on the ceramic paste. The thick reaction layers found in the glazes and the relative important amounts of ceramic paste diluted in the glaze do also indicate that it was applied over raw ceramic pastes. The lack of biscuit fired ceramics corresponding to the lead glazed production in the workshops do also agree with this.

The frits and related materials found in the workshop were used in the production of the tin glazes. The frit could be applied directly over the ceramic paste or mixed with sand, clay or other compounds to facilitate its application. Figure 4 shows chemical binary plots of the tin glazes, the ceramic pastes, the frit and the sand. We can see that the composition of the frit is very similar to the tin glazes, and that the differences may be explained by a small dilution of some ceramic paste in the frit. However, the potassium content of the glazes is too high and in some cases higher than the potassium content of the ceramic pastes. There is some documentation that indicates that salts were added to the frit before applying it onto the glaze (Perez Camps 1996). There exist also evidences of the addition of potassium and sodium salts to the tin glazes that were used in the production of lustre ceramics (Perez Camps 1998). These additions were made to facilitate the development of lustre decorations (Pradell et al. 2005). Therefore, we can assume that the high amounts of potassium in the tin glazes indicate the mixture of some salts to the tin glaze.

Finally, the use of biscuit fired ceramics in the production of tin glazed pottery agrees with the low

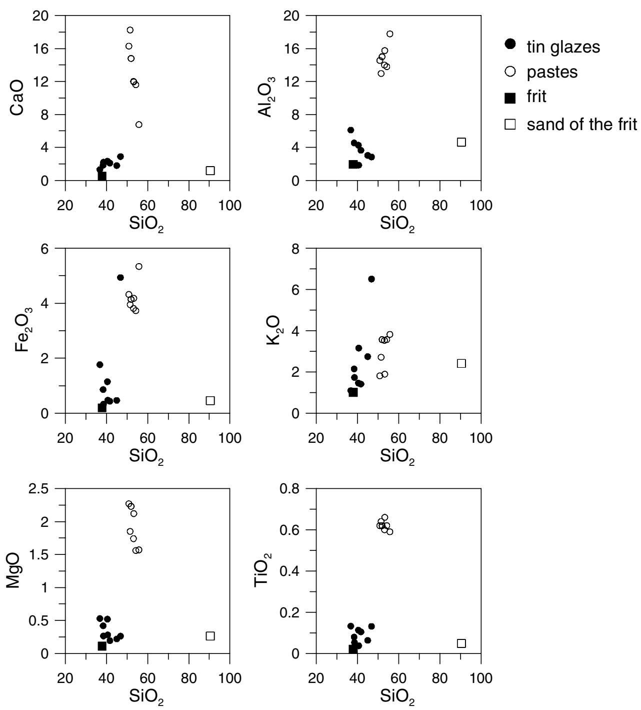


Figure 4: Binary chemical plots corresponding to the tin glazes and the corresponding ceramic pastes, the frit and the sand corresponding to the frit of the 13th century AD workshops from Paterna.

amounts of ceramic paste dissolved into the tin glaze. The large amounts of unglazed biscuit fired ceramics found in the workshops agree with this.

Available documentation (18th to 20th centuries AD) from Valencia and ethnographic studies of traditional pottery production in Spain (Valls David 1894; González-Marti 1952; Ferrís and Català 1987) indicate that medieval and modern frit processes are different. Since the 18th century the lead/galena and the tin were roasted in special kilns called *armeles* (Arabian word which means sand); this process takes 6 hours and the mixture needs a constant turning over. The final mixture consists in lead and tin oxides that mixed with sand and salt were fired directly in the fire chamber of the kiln, in an upper shelf named *sagen*. The main difference is that the 13th century AD Paterna craftsmen prepared the frits inside crucibles instead of melting them directly in the kiln. In both cases, a previous process of roasting galena is held and documents from 1520 (Gimeno Rosselló 1995) indicate the existence of an special kiln used to roast the lead/galena for all Paterna workshops.

The Islamic workshop of San Nicolás (Murcia)

The frits found in the islamic workshop of Murcia are related to the production of transparent and green "cuerda seca" lead glazes. The analysis of the materials found in the workshop indicates that the process for obtaining the transparent lead glazes, "cuerda seca" glazes and most probably the tin glazes is very sophisticated and consists of different steps. First, the lead ore, most probably galena (PbS) was roasted and a granular material made of lead oxides and some calcium-lead and lead silicates was obtained. This powder was mixed with sand (quartz) and introduced in the "orzitas" where it was fired in the kiln together with the ceramic production. The frit obtained was not fully molten and contained also quartz and calcium-lead and lead silicates. However this frit does not have the same composition as the lead glazes (see Fig. 5). On the contrary, the fragment of glass found in the workshop has the same composition as the lead transparent glazes. This suggests that the material obtained in the "orzitas" was ground and mixed with some clay (as the higher amounts of Al_2O_3, K_2O and Fe_2O_3 suggest) to obtain the transparent glass and with some copper to obtain the "cuerda seca" glass. The glasses were fired and molten in the cauldrons. The similarity in the composition between the lead glass and the lead glazes indicates that the ground lead glass was directly applied over the ceramic pastes.

The large amounts of biscuit fired pastes found in the workshop and the thin interfaces between the lead glazes and the ceramic body demonstrates that the transparent lead glazes were applied over biscuit fired ceramics. Moreover, as Figure 5 shows, the lead glass and the transparent lead glazes have the same composition and the dilution of paste into the glazes is very small.

Frits related to the tin glazes were not found in the workshop so we cannot draw conclusions about the technology of production of the tin glazes. However, the study of the glazes indicates also a double firing, small reaction layer between the paste and the glaze and a very uniform distribution of small cassiterite crystals in the tin glaze. All these suggest also a complex process that must involve a frit. Finally, we did not have "cuerda seca" fragments from the workshop and therefore we can not compare them with the green copper frits found.

The Persian Treatise (Allan 1973), dated from 1301, describes the production of frits in an Islamic workshop. The lead ore and tin were roasted together in a special kiln and the material obtained called "sirinj" has a sand consistency. The "sirinj" is mixed with roasted calcite and soda and fired directly in a special kiln from where the molten frit is poured into cool water. The archaeological findings from San

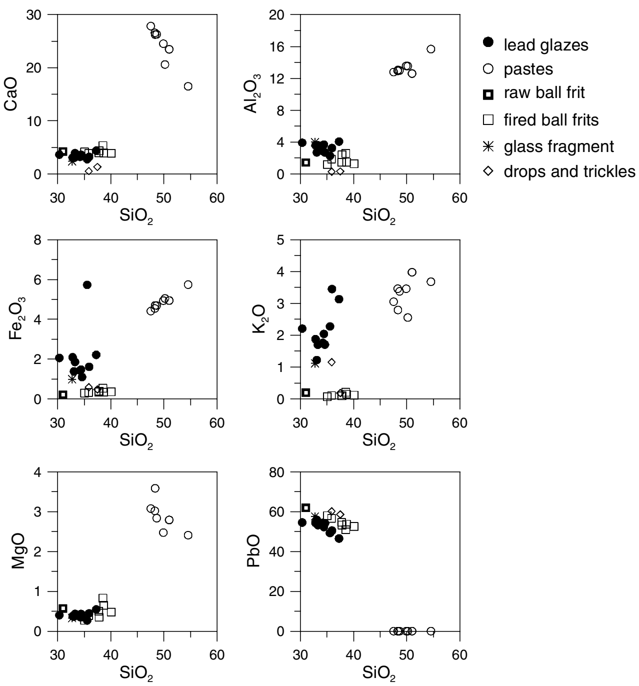


Figure 5: Binary chemical plots corresponding to the transparent lead glazes, ceramic pastes, raw ball frit, fired ball frits, glass fragment and drops and trickles corresponding to the 10th century AD workshop from San Nicolás.

Nicolás indicate a different process: the "orzas" were used to fire the "sirinj" and the cauldrons to modify the composition of the frits to obtain the different lead glazes and melt them.

Finally, while comparing the frits from Sant Nicolás and Paterna we can see a simplification in the process from the Islamic to the Hispano-Moresque productions. In San Nicolás all the glazes were fritted and the whole process included at least three steps, namely lead/galena roasting, firing of roasted lead and quartz in the "orzas", and melting of the frits with the final glaze composition in the cauldrons. In Paterna, although a previous process where lead/galena was roasted is presumable, frits were made only for the production of the tin glazes. The lead glazes were obtained by the direct application of the glaze material on the ceramic. And it is also worth to mention that although the process was simplified, the quality of the glazes was also very high.

Conclusions

The frits and related materials found in an Islamic workshop, San Nicolás (Murcia, 10th century AD) and an Hispano-Moresque workshop, Paterna (Valencia, 13th century AD) were studied. All the frits and related materials found in Paterna correspond to the production of tin glazes and there is no evidence for the use of frits in the production of the lead glazes. For the tin glazes a mixture of PbO, tin oxide and sand was fired in crucibles in the kiln. After cooling, the crucibles were broken to extract the fritted material which was ground and applied directly over the biscuit fired ceramic. A mixture of PbO, sand and an iron rich clay was applied over the raw ceramic and fired to obtain the lead glazes.

All the frits and related materials found in Sant Nicolás correspond to the production of transparent lead and "cuerda seca" glazes, while none of them is related to the production of tin glazes. However, the study of the tin glazes allows to assure that frits were also used in their production. A set of twelve "orzas" containing ball frits were analysed. The "orzas" were used to fire a mixture of quartz and lead oxides in the kiln. One of the ball frits contained the raw mixture of lead oxides and quartz sand and allows to assure that the lead/galena was roasted previously to its introduction in the "orza". After cooling, the "orzas" were broken to extract the material which was ground. This material was subsequently mixed with clay, copper, and other materials to obtain the final composition of the different glazes produced in the workshop, and the mixture was introduced into cauldrons where it was molten to obtain the glasses. Finally, the glass was ground and applied directly over the biscuit fired pottery.

The results of this study indicate that the fritting processes described in the literature do not correspond to the archaeological evidences. These processes were diverse in different workshops and geographical regions, and changed from early Islamic to Hispano Mudejar times.

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Notes

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Chapter 2

The emergence of ceramic technology and its evolution as revealed with the use of scientific techniques

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Abstract

In the long human evolutionary course 'technology' is initially limited only to the forming and shaping of existing natural materials. The production of new materials like ceramics presents the first technological revolution in human history which occurred only in the last 9000 years. It was most probably the result of the combination of two long-existing independent experiences: the pyrotechnology for burning limestone, and the moulding of raw clay. The scientific techniques developed and applied in the last 30 years have lead to remarkable discoveries about the knowledge of ancient potters. We now know how the pottery technology developed, how the raw materials were selected and treated, how the kiln atmosphere and temperature was controlled and how the different decoration colours and contrasts were obtained. This paper is an account of how our understanding about ancient ceramic technology developed with the progressive use of scientific techniques and methodologies. It begins with the very early attempts of potters to produce desired colours for the body and decoration and ends with the ingenious manipulation of materials, kiln atmospheres and temperatures to produce the high technology of black and red glosses in the Classical period.

Introduction

From the earliest stages of his appearance on earth, a couple of million years ago, man began his everlasting effort to comprehend and exploit the environment. His aim was initially to secure his survival and perpetuation and later the progressive improvement of his biotic level for a more comfortable personal life, and a more mature social life. From his first steps and for hundreds of thousands of years man shapes and uses the natural materials he finds in his surroundings, such as stone, timber, plants, bones, etc., for making tools, utensils, arms, clothes and lodgings, to obtain and prepare his food better and to encounter more comfortably the environmental conditions. The release of his hands with the development of the erect position helped him in such constructional attempts and at the same time contributed to the growth of an intellectual ability that lead him progressively to the manufacture of more and more complicated artefacts. In this long human evolutionary course the 'technology' is initially limited only to the shaping, however elaborate, of existing natural materials. The production of new materials is a relatively recent development and began about 11,000 years ago with the discovery of pyrotechnology, which was initially applied to the manufacture of lime and gypsum mortars (Kingery et al. 1988).

However, the grand moment in the technological development is the manufacture of the first ceramic, some 9,000 years ago in the Near East and a bit earlier in the Far East (Rice 1987). I believe humans achieved that by combining two long-standing and up to that moment independent experiences; a) their experience in pyrotechnology for burning limestone at temperatures above 800°C and b) their experience in moulding raw clay. They managed in this way to produce for the first time on earth a new material, the ceramic. The manufacture of this new material constitutes undoubtedly the first technological

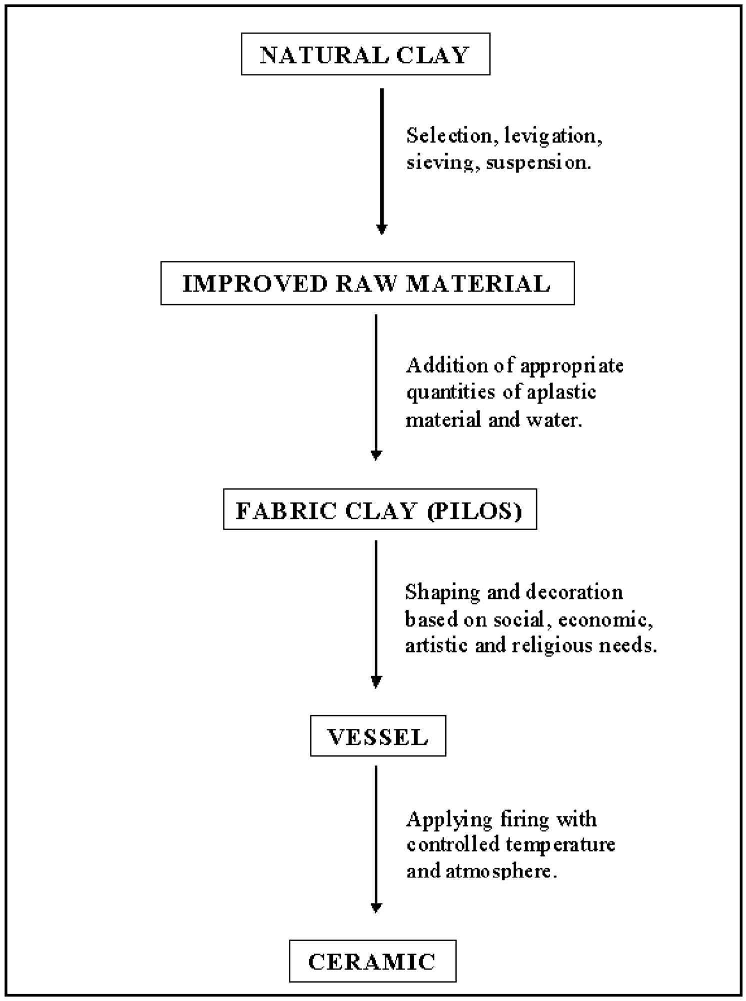

Figure 1: Stages and degrees of human intervention in the production of a ceramic vessel.

revolution in human history. This is because man, with the deliberate use of high temperature and long time heating, managed to alter the physicochemical properties of raw clay and thus to produce a new hard and durable material, ceramic. This was an unprecedented experience and a glorious moment in the course of human evolution. This first technological revolution was followed by a continuous development during which man manufactured progressively a lot of new materials. In the millennia that followed the ceramic revolution we witness the appearance of the vitreous materials (glazed stones, faience) technology, the appearance of metallurgy, a bit later of glass and so on. From then onwards the technological advancement becomes progressively faster, reaching an extremely high rate of evolution within the last 100 years when a large range of new materials are manufactured, amongst which are the polymers and the pure silicon on which the modern electronic industry is based.

Despite the large variety of new materials that are continuously produced until the present day, ceramics never stopped to be manufactured and improved, being strongly associated with the course of social and technological development until today.

The ceramic technology characterises and reflects important parameters of an ancient cultural society, as: 1) the organisation of society, including food preparation and storage, 2) the economy, 3) trade and commerce and 4) the connections and competitions with other societies. For this reason the investigation of the ancient ceramic technology is very important and its full understanding presents a challenge for Archaeometry.

It is worth refreshing our minds about how ceramic is manufactured and the degree of human intervention in each stage. The above diagram (Fig. 1) shows the successive stages in the manufacture of ceramic. The starting material is the clay, a natural sedimentary material that existed long before the appearance of man on earth.

The selection of a suitable NATURAL CLAY that contains a satisfactory percentage of argillaceous minerals, is relatively fine and has a good degree of plasticity constitutes the first step in the manufacture of ceramics. The next step involves the removal from the clay of the various accessory inactive and coarse-grained stone fragments. This is done by levigation, sieving and suspension in water. This process results in an IMPROVED RAW MATERIAL, very rich in argillaceous minerals and quite plastic. The refractory properties of this improved raw material need to be adjusted according to the type of ceramic product that is going to be manufactured. This can be done by adding, if necessary, calculated quantities of aplastic inclusions like quartz sand or crushed pebbles, feldspars, limestone, shells, or vegetal inclusions. A specific quantity of water is then added and the mixed material is manipulated either by wedging, kneading with hands or foot treading until it is fully homogenised and the air pockets removed. Thus the final clay composite material adapted for making pots is ready. We can call this final regulated clay FABRIC CLAY (Pilos). The next step involves the moulding and shaping of pilos to form the VESSEL. In the earlier periods, the vessel was constructed by shaping a clay lump with the hands or building it with the coil technique and later with the help of a wheel. The vessel could then be painted or decorated. The stage of forming and decoration of a vessel is very important, as in the form and decoration all parameters that are characteristic of an ancient society are reflected. Such parameters are: 1) the dietary habits, the needs for storage and commerce (cultivation, accumulation of goods, exchanges, economy), 2) the needs for social and artistic practices, 3) the needs of religious worship and 4) effects that emanate from possible social class differentiations (variable accumulation of wealth, specialisation of potters, access to raw materials, etc.). The shaping and decoration of the vessel is followed by the firing stage. The firing causes permanent physicochemical changes to the natural clay material. Initially and at low temperatures (100–200°C) only the absorbed water is involved. As the temperature increases (400–800°C) the chemically bound hydroxyl (OH) water is removed, a process associated with the disorganisation of the clay minerals. With a further rise of temperature (800–1000°C) solid-state reactions begin to take place during which new minerals may appear with the simultaneous formation of an amorphous phase (vitrification), which consolidates and cements the particles together. This whole process converts permanently the natural clay to a CERAMIC.

The firing of ceramics requires specific skills for reaching and maintaining firing temperatures in the range of 800–1000°C, know-how for building kilns, control of air, and it generally reflects the technological level of a society at a specific period and place. It is therefore obvious that the investigation of the ancient ceramic technology with modern scientific methods provides invaluable information on all the aspects of technological development but also on aspects that are related to the economic, social, and religious life of man. Methodologies for the study of ancient ceramic technology began to be developed in the 1960s, based on Powder X-ray Diffraction (Perinet 1960), Thermal Expansion (Cole and Crook 1962; Tite 1969), and optical microscopy (Cowgill and Hutchinson 1969). In the next decade (1970s), new methods are added, based on Mössbauer Spectroscopy (Bouchez et al. 1974; Janot and Delcroix 1974), Ceramic Hardness (Fabre and Perinet 1973), Differential Thermal Analysis (Kingery 1974; Slager et al. 1978), Porosity (Morariu et al. 1977), and Scanning Electron Microscopy (Tite and Maniatis 1975; Maniatis 1976; Maniatis and Tite 1978/9). The next decade (1980s) witnessed the further development of the methodology based on the Analytical Scanning Electron Microscopy that was destined to dominate ancient ceramic technology studies. With this method, a deeper understanding of the effects of firing on the different types of clay used for making ancient pottery (Maniatis and Tite 1981) and information contributing to the qualitative and economic elements of a society is extracted (Maniatis et al. 1988). Today we understand most of the parameters related to ancient ceramic technology and the techniques of ceramic decoration and we are in a position to appreciate the degree of difficulty, the specialisation and the know-how that existed in the manufacture of many types of ceramics in various periods and cultures. This is the result of the continuous development and systematic application of Materials Science methodologies and the progressively accumulated experience by dedicated archaeological scientists (Archaeometrists). The investigation of the thermal behaviour of raw materials in combination with the cultural context and the absolute chronologies of the findings have provided information not only on the ceramic technology itself but also on the conditions that preceded this technological revolution.

The opinion I formulated earlier, that man achieved the production of the first ceramic when he combined, at a certain moment in time, two of his long-standing previous experiences; his art in shaping the raw clay and his knowledge in pyrotechnology, is based on results produced by the application of scientific techniques. For example, it has been proved that man had acquired the knowledge to process and mould clay long before the firing of ceramics. In particular, objects of refined, worked and shaped but unfired clay, identified using X-Ray Diffraction and Analytical Techniques, were found in various parts of the world. Some examples are the famous clay figurines found unfired and subsequently fired (most probably accidentally in a destruction fire) from Dolní Vestonice in Slovakia, dating to 30,000 BC (Zimmerman and Huxtable 1971). Other examples are the cylindrical clay rods, dating to 12,000 BC, from the cave Theopetra in Thessaly, Greece (Facorellis et al. 2001), which are considered the oldest clay objects in the Greek region. It is certain that the evidence would have been much richer, but, as the clay objects were unfired, could not have survived to our days. At the same time, it has been proven that humans, long before the manufacture of the first ceramic, possessed the knowledge to obtain and maintain temperatures above 800°C in large volumes. Indeed, examination of different mortars using electron microscopy, from settlements in Mesopotamia, dating 10,000–9,000 BC, showed that they consisted either of calcium carbonate ($CaCO_3$) or gypsum ($CaSO_4.x H_2O$) particles. The small particle sizes (a few micrometers) and their characteristic microcrystalline forms indicated secondary crystallization in-situ on the wall after the application of the mortar (Kingery et al. 1988). This obviously implied combustion of natural limestone and gypsum rocks at temperatures above 800°C in order to evoke the dissociation of the natural rocks and the production of lime ($Ca(OH)_2$) and anhydrous gypsum ($CaSO_4$) from which the corresponding mortars are manufactured. The firing of limestone and plaster requires similar skills and logic to the firing of the ceramics; i.e. the firing temperatures are more or less the same, they should be uniform in large volumes (in specially built bonfires or kilns) and they should be maintained constant for a long time interval (a few hours).

Thus the conquest of the ceramic technology came as a reasonable consequence of a clever combination of the above two long-standing and independent experiences. For this reason the first ceramics, when they appear in Mesopotamia, are well made and fired at suitable temperatures (850–950°C) to produce enough sintering and vitrification for durable ceramics. This has been shown by the solid-state reactions that have occurred between the clay minerals in their body and the development of amorphous phase, observed by scanning electron microscopy and X-ray diffraction (Tite and Maniatis 1975; Maniatis 1976).

Firing temperature, microstructure and mechanical properties

There are various scientific methods that can be used to get an estimate of the temperature at which a ceramic has been fired (Heimann and Franklin 1979; Tite 1995). These are based on: 1) mineralogical changes occurring in the clay body during firing, monitored with powder X-ray diffraction (XRD) (Maggetti 1982), thermal expansion (Tite 1969), differential thermal analysis (DTA), thermogravimetric analysis (TGA) (Kingery 1974), Mössbauer spectroscopy (Maniatis et al. 1982; Wagner et al. 1986), infra red spectroscopy (FTIR) (Maniatis et al. 2002), etc. 2) colour changes (Matson 1971) and 3) sintering and vitrification, monitored with thin-section optical microscopy, hardness, porosity changes and scanning electron microscopy, or the combination of the above methods. The firing temperature is not a strictly defined term because the firing rate and soaking time affect the mineralogical changes and the degree of sintering and vitrification. It has been estimated that firing at 960°C with a fast heating rate of about 800°C/hr followed by rapid cooling, conditions similar to that obtained in a bonfire (Shepard 1956), would create the same effect on vitrification as that obtained with firing at 900°C with a slow heating rate of 200°C/hr and 1 hour soaking time (conditions comparable to firing in a kiln). Thus shortening the total time of firing from a day that is the usual situation with kiln firings, to just 2 hours, increases the effective temperature by 60°C (Maniatis 1976). Similar results are obtained when the soaking time at the top temperature decreases by 5-fold (e.g., from 300 min to 5 min) (Norton and Hodgdon 1931; Maniatis 1976) and when the atmosphere changes from reducing to oxidising (Maniatis and Tite 1981). Comparable results are also obtained for the mineralogical changes occurring during firing at lower temperatures monitored with FTIR, the equivalent temperature being higher by 50–60°C when the soaking time decreases by 5-fold (Maniatis et al. 2002). For this reason it is better when one refers to firing temperatures usually refers to the "equivalent firing temperature", i.e. equivalent to the heating rates and soaking times obtained in a kiln (Tite 1999).

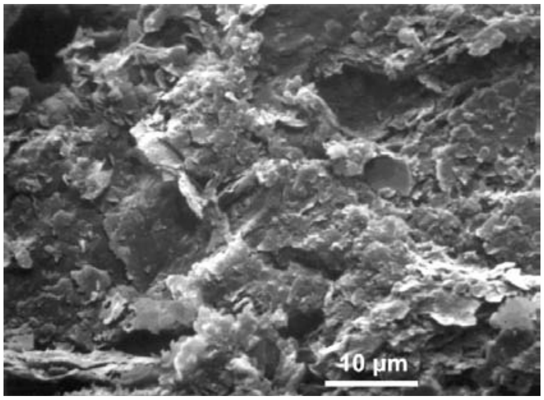

Figure 2: SEM secondary electron image of an unfired clay vessel (fractured surface). The clay flakes can be clearly seen.

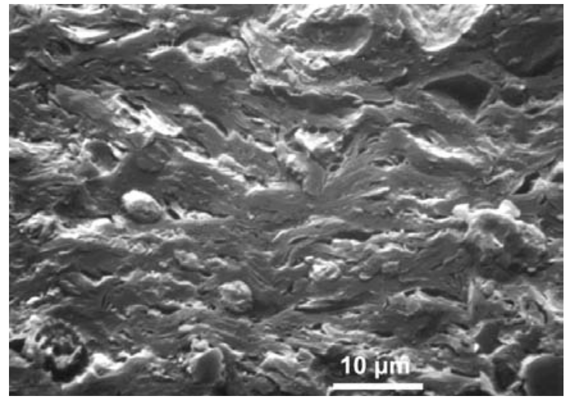

Figure 3: SEM secondary electron image of clay vessel fired at 930°C (fractured surface). The vitrification in the form of smooth glass wavy strips is evident.

There are many applications on a large number of ancient ceramic groups of different periods and locations, through which estimates, as good as possible, of the original firing temperatures employed have been obtained. However, it has been argued (Gosselain 1992) that the firing temperature by itself does not mean very much neither for assessing the ancient ceramic technology nor for extracting cultural and behavioural information concerning the production and use of ceramics. Indeed, the temperature estimation should be combined with determinations of the chemical composition, the refractory potteries and the tempering of the clay used. Only in this way the level of understanding of the raw materials and their behaviour on heating by the ancient potters can be assessed. A method that was developed since the mid seventies and found very interesting applications in the study of ancient ceramic technology is the analytical scanning electron microscopy (SEM-EDXA). This method is based on estimating the degree of sintering and vitrification (glassy phase) that is observed in the microstructure of a ceramic (Maniatis and Tite 1975; Tite and Maniatis 1975a; Tite and Maniatis 1975b; Maniatis 1976; Maniatis and Tite 1981). For example, Figure 2 shows the micromorphology of the body of a clay vessel that has not been fired, as seen under the SEM and at a magnification of 2000x. The characteristic flakes of the raw clay can be clearly seen. Figure 3 shows the microstructure of the same clay vessel now fired at 930°C under oxidizing conditions (all vents of kiln open). The amorphous phase takes the form of wavy strips of glass developing as a result of sintering and melting of the edges of the parallel-orientated clay flakes. The progressive sintering and vitrification helps the adhesion and cementing of the particles together, a process which converts the natural clay to a ceramic.

The development of scanning electron microscopy in combination with microprobe X-ray analysis contributed a lot to the understanding of the effect of firing on natural clays and the factors that influence the progressive changes in their microstructure. It is now known that the sintering of clays during firing occurs with the transfer of material to the contact surface between the particles (Fig. 4a) through a process of 'plastic flow' (mobilization of molecules without full melting) (Kingery et al. 1976). The development of a glassy phase (vitrification) is independent of the sintering. However, the appearance of the vitreous 'liquid' phase increases the surface tension between the clay particles, and this creates a lower pressure in the contact surface and hence the appearance of attractive forces that draw the particles together (Fig. 4b), leading to the familiar contraction of the ceramics during firing. Vitrification appears as continuous glass filaments at first, joining the edges of the parallel aligned clay particles, and later as wavy glassy strips (Fig. 4b) when the filaments from several

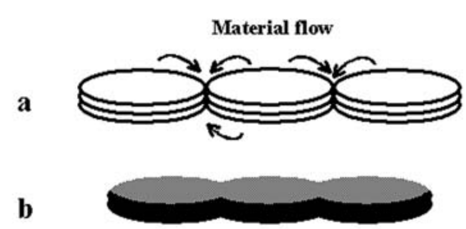

Figure 4: Layers of clay flakes aligned parallel as in a clay vessel, a) during heating material flows to the contact edges of the particles, b) melting occurs at the edges creating wavy strips of glass. The particles are drawn together resulting in sintering and contraction.

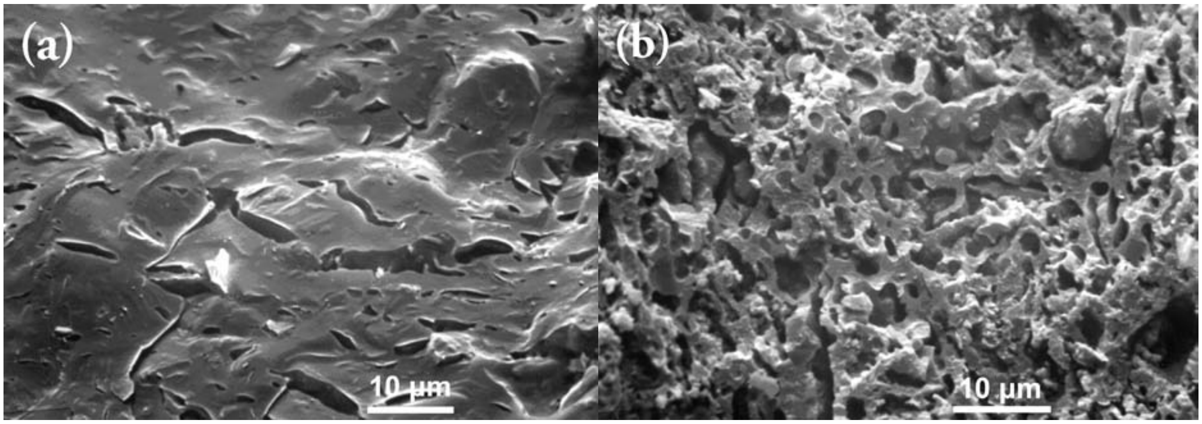

Figure 5 (a): SEM secondary electron image of a non-calcareous ceramic fired at 1000°C (fractured surface) – Totally vitrified matrix. (b): SEM secondary electron image of a calcareous ceramic fired at 1000 °C (fractured surface) – An open cellular porous matrix.

clay layers fuse together. This process can be monitored very precisely with the SEM as can be seen in Figure 3. The temperatures at which the above changes occur, the amount of glassy phase developed, the pattern the vitrification exhibits in the clay matrix and the degree of contraction, depend on the chemical and mineralogical composition, and the particle sizes. It also depends on the amount, type and size of accessory minerals and aplastic inclusions. Figures 5a and 5b show the dramatic differences, revealed with the SEM, in the microstructure between a ceramic made of a clay low in calcium (CaO = 0–2%) clay and a ceramic made of a clay high in calcium (CaO = 15%), both fired at the same temperature (1000°C). The calcareous ceramics, containing CaO > 6% in a fine calcium carbonate form, exhibit a characteristic cellular structure with a high porosity (Tite and Maniatis 1975) and at the same time the vitrification is more restricted and controlled up to 1150°C. This characteristic microstructure remains constant for 200°C (850–1050°C) and above that there is a progressive increase of vitrification, the glass phase becoming grainy and highly viscous (Tite and Maniatis 1975; Maniatis 1976). Contrary to that, the non-calcareous clays, containing CaO < 6%, produce a much more vitrified ceramic body with a high density and impermeable to fluids. Furthermore, due to the extensive and rapid vitrification the non-calcareous ceramics collapse at temperatures approaching 1100°C (Maniatis 1976). The calcareous ceramics have a greater resistance to thermal and mechanical shocks due to their highly porous microstructure (Kingery et al. 1976), as the energy is absorbed by the voids, but they have lower resistance to loading and compression, as they are less rigid.

Hence, the examination of the ceramic microstructure under the analytical SEM provides information on the degree of vitrification that leads to the estimate of the firing temperature but at the same time on the chemistry and type of clay used and its refractory properties (Maniatis and Tite 1981). Important information is thus extracted on the level of apprehension by the ancient potters of the properties of different clays. This in combination with the raw material availability in a certain region and its use for specific types of ceramic ware leads to a deeper understanding of the level of ancient ceramic technology and the social and economic implications related to it (Maniatis et al. 1988; Tite 1999).

The mechanical and thermal properties of ceramics can be strongly modified by introducing aplastic inclusions whose concentration and size strongly affect these properties. Such inclusions may be fragments of quartz, feldspars, limestone, seashells etc. Their role is quite important in preventing extensive cracking by the stresses developing during the drying shrinkage, especially in thick walled vessels like *pithoi*, but also in increasing the toughness (prevent breakage by cracking) of the ceramic during loading. Figure 6a and 6b show in diagrammatic form how the cracks developing initially in the vicinity of an inclusion (Fig. 6a) are widened during drying (Fig. 6b). The energy of the widened cracks is absorbed in the void of the inclusion, which in this way prevents the cracks extending from one surface of the vessel to the other. In the same way a crack propagating in a ceramic containing quartz inclusions is absorbed by bending and its propagation stopped by the inclusions (Fig. 7). The role of inclusions in the mechanical and thermal properties of ceramics has been the

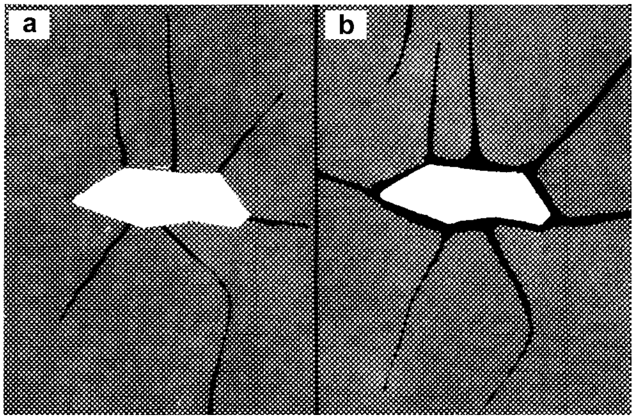

Figure 6: Crack propagation, a) cracks propagate to the inclusion, b) cracks become wider during drying but their energy is absorbed around the void of the inclusion.

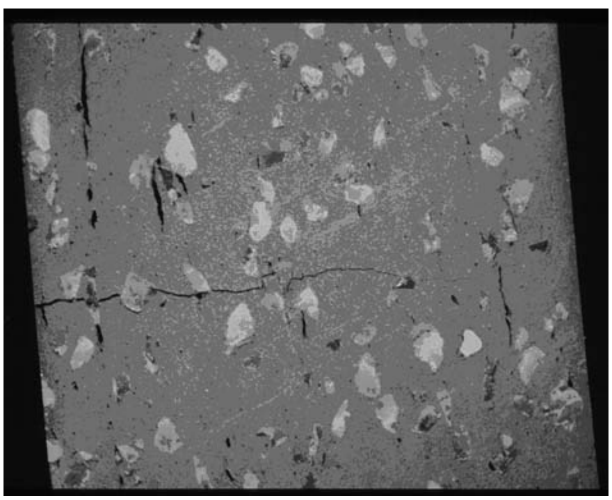

Figure 7: Crack created and propogating (from left to right) under mechanical bending in a ceramic containing quartz inclusions.

subject of extensive research in recent years (Kilikoglou et al. 1998; Vekinis and Kilikoglou 1998; Tite et al. 2001).

Colours of body and paint in oxidising conditions

The systematic applications of microanalysis, mineralogical studies and Mössbauer spectroscopy in combination with magnetic measurements contributed greatly to the better understanding of the parameters controlling the colour differences between the different ceramics and the utilization of these properties by the ancient potters to produce various aesthetic and functional results. It is now known that the colour exhibited by a ceramic is a result of the chemical composition of the clay and the firing conditions (temperature and atmosphere). The iron oxides play a very important role in the colour of the fired ceramic and influence also the colour of the natural raw clay. Initially in the raw clay, iron is in the form of iron hydroxides, such as FeO(OH), that are orange or brown in colour and fine iron trioxide (Fe_2O_3), which is red/brown in colour. Some Fe is also bound in the form of ions Fe^{3+} or Fe^{2+} in the structure of the clay minerals that are colourless. The combination of the different forms and quantities of iron existing in a clay together with the quantity of organic material contained gives a variety of colours to the raw clays, which range from grey, beige, brown, orange, or red.

When a clay is fired the colours change depending on the temperature and atmosphere, but the presence of fine calcium carbonate in the raw clay plays again, as in the development of micromorphology, a very essential role to the final colour. In non-calcareous clays fired at oxidising atmosphere (all vents of kiln open), there is a progressive crystallisation of Fe in the form of alpha-Fe_2O_3 (haematite), which is red in colour. These oxides grow in size and quantity as the firing temperature increases above 700°C at the expense of the Fe-hydroxides and the Fe-ions in the clay mineral lattice, which begin to disorganise and dissociate above that temperature, liberating Fe ions (Maniatis et al. 1981; Maniatis et al. 1982; Maniatis et al. 1984). As a result, the non-calcareous clays fired at oxidising atmospheres exhibit red colours, which become more intense as the firing temperature increases. Contrary to that, the reactions occurring during firing in the calcareous clays (fine CaO > 6%) are quite different. The CaO that appears from the dissociation of calcium carbonate above about 750–800°C, reacts strongly with the iron oxides and breaks them down. This leads to the decrease in size and amount of Fe-oxide particles and hence to the bleaching of the red colour to pink, cream or even whitish as the temperature increases above 850°C and according to the original amount of calcium carbonate in the clay. The Fe which is liberated from the dissociation of iron oxides participates in the crystallisation of new calcium aluminosilicate minerals (Maniatis et al. 1981) which stabilise the microstructure of the calcareous clays for 200°C (850–1050°C). These new minerals are colourless. Exceptions to this general behaviour do occur. For example, there are calcareous clays that are red from the beginning and remain red after firing, because the original amount and particle size of the iron oxides

present is so large that the CaO is not enough to react to a considerable degree as to bleach the colour (Maniatis et al. 1981); equally, there are some non-calcareous clays that fire to whitish colours because the initial amount of iron oxides they contain is very small. The latter are usually the high refractory kaolinitic clays (Maniatis and Tite 1978-9).

These colour differences between the various clays were cleverly utilised by the ancient potters from Neolithic times. They used these different clay properties in order to produce decorative colour contrasts with a single firing. An example is shown in Figure 8 where a beautiful red coloured decoration has been applied on a buff coloured body. This result was achieved by using a highly calcareous clay for the body and a non-calcareous fine clay for the decoration paint, fired in an oxidising atmosphere at a temperature of 900°C. Judging from the final fired colours and based on recent experience accumulated on various raw clays one can say with a fair degree of certainty that the initial raw colours for the two clays used for this vase in Figure 8 must have been: light grey for the body and orange or red for the paint. The manufacturing of such a vase required a selection and refinement of raw materials, as well as uniform oxidising firing, features that are associated with production of high quality pottery. Pottery of the same kind, with red 'flame-like' decoration on buff body, was found in the Middle Neolithic period at Sesklo, Thessaly among other monochrome vases. The scientific investigation using analytical SEM showed that this pottery was indeed of high quality requiring the use of a special calcareous clay that was not available in the immediate vicinity of the site and a specially treated non-calcareous clay for the red decoration. Furthermore, this pottery was fired at such conditions as to take full advantage of the specific clay properties. The same was not true for the rest of the pottery found at the site or in a nearby site (Sesklo B) that was dominated by the monochrome lower quality pottery (Maniatis et al. 1988). Therefore, this high quality pottery required skillful and specialized potters most probably not producing their own food, probably implying a central economic system that distributed wealth (Kotsakis 1983).

Figure 8: Red on buff decoration on a Neolithic Period vessel from Thessaly, Greece.

Colours in reducing conditions

Firing pottery in reducing conditions (lack of oxygen and presence of reducing gasses, such as CO in smaller or larger amounts) produces different results. The Fe-hydroxides and Fe-oxides existing in the raw clay dissociate during firing under reducing conditions above about 700°C and by liberating oxygen they are progressively converted to magnetite (Fe_3O_4) or wüstite (FeO) or even rarely to metallic iron depending on the intensity of the reducing conditions and the firing temperature. Both magnetite and wüstite are black in colour while metallic iron has a dark metallic shade. Furthermore, wüstite is a very strong flux and its presence in the clay matrix at temperatures above 800°C can lead to intense solid-state reactions with the argillaceous clay minerals. This results in an increased vitrification and rapid drop of the viscosity of the glass phase. The dropping glass viscosity in combination with the liberation of oxygen from the dissociating iron oxides creates bloating in the microstructure. The bloating pores clearly seen with the SEM (Maniatis and Tite 1975) increase in size with the firing temperature and this leads very soon to the swelling and deformation of the vase and finally to its collapsing. Thus the conversion of iron oxides from their oxidized form to the reduced one produces in general dark ceramics and glass with low viscosity and bloating.

However, this is not always the case. The presence of fine calcium carbonate in the clay is again very important for the properties of the ceramic such as microstructure, vitrification, bloating, and the final colour. In the non-calcareous clays firing in a reducing atmosphere produces dark grey to even black colour ceramics, while in the calcareous ones reducing firing produces light grey to even whitish colours. The difference is due to the fact that in the calcareous clays the CaO reacts with the Fe-oxides and as in the case of the oxidising conditions, it forms new Ca-Fe-aluminosilicate minerals (Maniatis et al. 1983). This absorption of Fe into new minerals does not favour the crystallisation of the reduced black iron oxides (magnetite and wüstite), and so the colours of the calcareous ceramics fired in reducing conditions range from pale grey to whitish (CaO > 15–20%) according to the initial amount of calcium carbonate and the firing temperature. The decrease in the production of FeO in the calcareous ceramics, apart from the colour, has an important effect in the properties of these ceramics. The uncontrollable production of low viscosity glass in the microstructure is stopped and the bloating is largely reduced (Maniatis and Tite 1975), preventing in this

way the deformation and the collapsing of the vessel, even at higher temperatures.

For the colour of ceramics fired in reducing conditions, it should be noted that the differences between calcareous and non-calcareous clays emerge only above 800°C, because the dissociation of $CaCO_3$ and the appearance of the reactive CaO in the clay matrix occurs at about this temperature. Firing at temperatures below 800°C does not produce any difference in the colour or the properties of the ceramics. The colours in this case are all dark grey irrespective of the clay chemistry. Figure 9 shows an indicative diagram for the colours developing in calcareous and non-calcareous ceramics during firing in a reducing atmosphere. The curve of non-calcareous clays is only theoretically extended to 1100°C, because, as discussed above, such a ceramic cannot survive above 950°C in reducing conditions. However, when a non-calcareous clay is heavily tempered it can resist higher temperatures in reducing conditions. An example are the high density, strong and impermeable bodies of a class of dark coloured Punic Amphorae found at Corinth (5th century BC), containing quartz, feldspar, mica schist but also some limestone inclusions (Maniatis et al. 1984).

The reducing conditions during firing of the ceramics can be created by closing all the openings of a kiln and throwing some fresh wood in the fire compartment or by firing in ground pits and covering all the vessels with straw and wood or with larger vessels (*pithoi*). Sometimes reducing conditions can be created at a certain point inside a kiln or a bonfire accidentally, due to bad air circulation. A lot of dark coloured ceramics, some nicely burnished, are observed in the Neolithic and Early Bronze Age Period in many parts of the world and they are the result of firing in ground pits covered with straw, wood and perhaps soil on top. These vessels are typically made of non-calcarous clays and fired at about 800°C or even sometimes of calcareous clays but fired below 800°C so that the calcium carbonate does not dissociate. The reducing firing is surely intentional and the dark coloured ceramics represent a certain tradition. However, the firing conditions are not easily controlled and for this reason a lot of ancient ceramics are partially grey and partially red (Fig. 10). At about the Middle Bronze Age (1900 BC), grey uniform ceramics fired in reducing atmosphere but certainly in kilns are produced in many parts of Greece. Typical examples are the so-called 'Grey Minyan' ceramics (Fig. 11), the best of which are made of a highly calcareous clay, fired at about 950°C. They have a uniform light grey colour and a characteristic soapy feel due to the very fine calcareous clay from which they are made.

Black decoration on a light background

The black decoration on a light body (red, pink, crème or white) represents a further advancement in ceramic technology. In order to produce a red or light colour body the ceramic needs to be fired under oxidising conditions. In this case, however, if the decoration paint were made of a fine clayish material its colour after an oxidising firing would be red or pink, like the example of Figure 8. Thus, in order to achieve a black decoration on a reddish or whitish body a material other than clay should be used. This material must be black and should stay black after firing in an oxidising atmosphere.

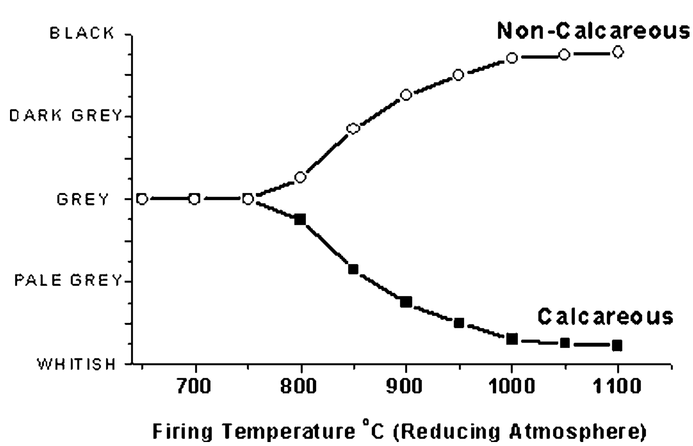

Figure 9: Diagram indicating the development of colours in non-calcareous and calcareous ceramics fired under reducing conditions.

Figure 10: Neolithic dark coloured (dark burnished) vessel made of non-calcareous clay fired in reducing conditions at about 800°C. The bottom part is either intentional or accidentally oxidized.

Figure 11: Middle Bronze Age 'Minyan pottery' made of a highly calcareous clay fired in reducing conditions at about 950°C. Compare the light grey colour due to the presence of CaO with the dark colour of figure 10.

Typical materials for this technique are the natural manganese ores used during the Neolithic and Early and Middle Bronze Age (Noll 1982). Such ores are the MnO_2 either in pure crystalline form called pyrolusite or in a colloidal form known as psilomelane, the latter sometimes containing also barite ($BaSO_4$). These manganese oxides are originally black and remain black after firing in oxidising conditions. Sometimes Fe-Mn ores are used which also contain small quantities of clay (Noll et al. 1975; Aloupi and Maniatis 1990; Kilikoglou et al. 1990), which helps to adhere the paint better on the vessel's surface. In this case the colour of the decoration at higher temperatures can come out dark brown rather than black. Therefore using manganese oxide pigments for the decoration, it is relatively easy to obtain the contrast of a black or dark brown decoration on a light body. The body can be made of calcareous clay and the vessel fired in oxidising conditions at temperatures in the range of 800–900°C. Using the manganese oxides polychrome decorated vessels could also be obtained (Fig. 12). In this case manganese oxide is used for the black decoration, non-calcareous refined clay for the red decoration and calcareous clay for the body (Aloupi and Maniatis 1990; Kilikoglou et al. 1990). A single firing at an oxidising atmosphere is enough to produce this polychrome result. However, the black coloured decoration obtained with manganese pigments is not in general of very good quality, because it is relatively coarse and does not sinter in the usual firing temperature ranges (850–1050°C). As a result, the paint has a matt appearance without any sheen, despite the polishing efforts obvious in some cases and has a bad adherence with the body being rubbed off by the hand quite easily.

During the end of the Middle Bronze Age but especially during the Late Bronze Age, a black paint of a much superior quality appears, produced with the so-called iron reduction technique involving the reduction of iron oxides in the paint. The understanding and deliberate use of this technique by the ancient potters represents a big step forward in the ceramic technology evolution. For the production of this black paint a very good control of the kiln is required, with a precise closing and opening of the vents in order to change the atmosphere in the kiln from oxidising to reducing and then back to oxidising at specific temperatures and times. In this way a black glossy decoration is produced on a light body background. With the application of scientific techniques it was possible to reveal the complicated technology involved in the manufacturing of the black gloss decoration, using the iron reduction technique (Hofmann 1962; Noll et al. 1975; Tite et al. 1982; Aloupi and Maniatis 1990; Kingery 1991; Aloupi 1993; Maniatis et al. 1993), and to establish that this technique reached an extremely high level of technology during the Classical Period in Attica. This was the period when the famous Attic Black Figured and Red Figured vases (Fig. 13) were manufactured and acquired a very high artistic and commercial value, being traded all over the ancient world of that period. The analytical scanning electron microscopy proved once again a powerful tool for the extraction of invaluable technological information. Figure 14 shows the micromorphology of the black gloss paint and the ceramic body of an Attic vessel at a cross section. The black gloss layer exhibits a high degree of uniformity and sintering. The amount of vitrification is optimum so that the layer is quite dense and

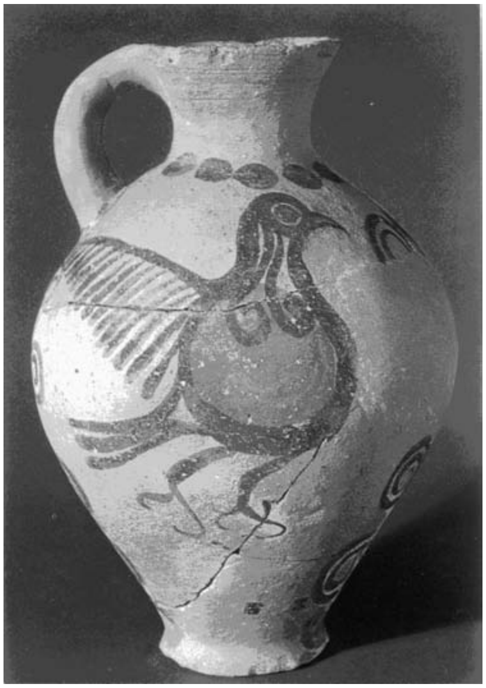

Figure 12: Vessel from Akrotiri, Thera bearing Mn-black decoration. The red decoration is made of fine non-calcareous clay. The body is made of a highly calcareous clay. It is fired in an oxidizing atmosphere.

Figure 13: Red figured Attic vase. The black paint is produced with the iron reduction technique.

perfectly bonded to the body but at the same time does not show any deformation or bloating. The ceramic body exhibits an open cellular microstructure characteristic of a calcareous clay fired in the range 850–1050°C. In the next figure (Fig. 15) one can see the micromorphology of black paint from earlier periods (LBA), when the first attempts to produce black paint on light body using the iron reduction technique began (Aloupi and Maniatis 1990). The differences with the Attic black gloss are apparent. The vitrification of the LBA black layer is excessive; the viscosity of the melted paint has dropped dangerously with the simultaneous appearance of bloating and deformation, resulting in a lower quality product. Actually, this outcome is the most frequent result when there is no absolute control of the firing conditions in the kiln (atmosphere and temperature) or/and of the selection and treatment of the raw materials.

A comparison of the chemistry between black glosses of different periods, from Early Bronze Age to the Classical period (Table 1), shows the improved refinement of the paint material with time as witnessed by the progressive removal of Ca and the increased ration of Al/Si, from 0.45 to 0.61 and finally to 0.67 in the classical period.

For the high quality black gloss paint, like the one on the Attic vases, a carefully selected and thoroughly treated clay is needed, as well as a fully controlled three-stage firing. The raw material to be used for the paint should be practically free of calcite (CaO < 1%), enriched in fine clay minerals, potash and iron oxides. This can be achieved by the selection of a fine illitic and calcium free clay and then by a persistent suspension in water for months. During the prolonged suspension the aplastic and coarser particles, like quartz, feldspars, aggregates etc., are removed and the suspended fraction is enriched in very fine argillaceous minerals (mainly illite) and very fine iron hydroxides or/and iron oxides that give to the raw paint an orange to red initial colour. The selection and treatment of the raw materials can be seen in Figure 16 that shows the iron concentration, important for the colour, against the Al/Si ratio that indicates degree of refinement. The consistency in chemistry and treatment is remarkable, particularly for the black gloss paint.

The examination of the black gloss paint on Attic vases with the transmission electron microscope (TEM), at high magnifications, gave important information on the grain sizes and the firing conditions (Maniatis et al. 1993). The black paint seems to contain mainly magnetite (Fe_3O_4) crystals, as was verified with electron diffraction, that are dispersed

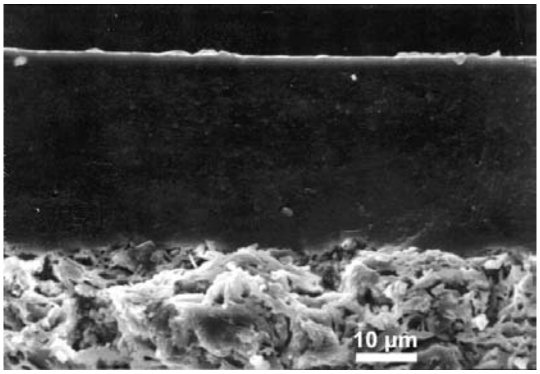

Figure 14: Micromorphology of the black gloss of an Attic red-figured vase (6th cent. BC) at a cross section near the surface. The unique homogeneity of the sintered and compact black gloss layer adhering nicely to the porous calcareous body is evident. SEM image at secondary electron mode.

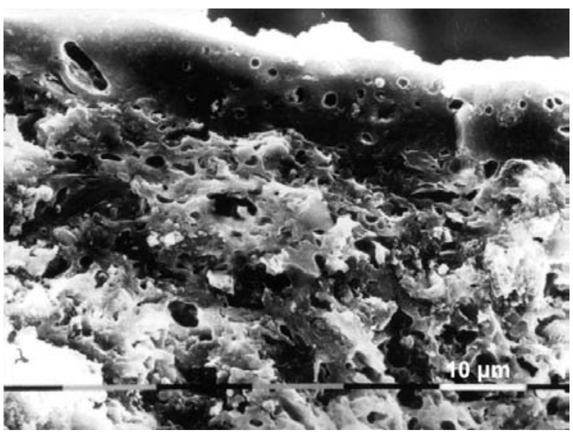

Figure 15: Micromorphology of a much earlier (1600–1500 BC, Thera) black paint produced with the iron reduction technique, at a cross section near the surface. The black layer is grainy, with bloating pores and deforming. The body is again calcareous and porous. SEM image at secondary electron mode.

inside an amorphous matrix (Fig. 17). Magnetite has a black colour and its presence gives the paint its characteristic black colour. As was discussed earlier, magnetite does not exist in the raw clay but it is produced from the dissociation of haematite during firing in reducing conditions. It is therefore clear that at some stage of the firing the atmosphere in the kiln was reducing. Furthermore, the affluent presence of magnetite suggests that the reduction stage was mild and controlled so that the dissociation of haematite practically stopped after conversion to magnetite and did not progress further to produce large quantities of FeO. The latter is very reactive and if present would lead to rapid vitrification with inevitable bloating and deformation as in Figure 15. Contrary to the reducing firing verified for the black paint, the ceramic body is fired in oxidising conditions as is deduced from its pink colour. These results clearly indicate an alternation in the kiln's atmosphere from oxidising to reducing and vice-versa. As far as the grain sizes of the paint material are concerned, the greatest size of original particles typically found in the Attic black gloss are some rare titanomagnetite particles (a rather common aplastic accessory mineral in a lot of clays) of dimensions of 0.0003 mm (Maniatis et al. 1993). Thus, from the TEM examination it is confirmed that the refinement of the clay used for the paint was extremely persistent.

The above scientific conclusions inferred from the examination and analysis of the attic black gloss were tested thoroughly with simulation experiments in the laboratory (Aloupi 1993). These experiments suggested that the optimum three-stage firing cycle must have been as follows:

Stage 1: Initial firing in oxidising conditions up to about 900°C and soaking at top temperature for an hour or more.
Stage 2: At the top temperature creating reducing conditions by closing all the vents of the kiln and feeding the fire with fresh wood, most probably wet. Inevitably and wilfully the temperature drops a couple of hundred degrees to about 700–750°C.
Stage 3: Opening again all the kiln's vents and new increase of temperature up to about 850°C for an hour and then cooling, maintaining the oxidising conditions until the end.

In the first oxidising stage, the body of the ceramic becomes pink since it is made of calcareous clay. The paint becomes intense red as it contains no calcium carbonate and it is rich in iron, the latter forming well-crystallised haematite particles. At this stage a controlled sintering and densification occurs in the paint layer.

In the second stage, that is reducing, haematite is transformed to magnetite and as a result the colour of the paint becomes intense black. The body colour becomes grey as all calcareous clays (see diagram of Fig. 9). This stage is very critical because if the control of temperature or atmosphere is lost to more intense reducing conditions, magnetite may dissociate further to wüstite, leading to rapid vitrification and melting of the paint layer as discussed earlier. On the other hand if the atmosphere swings to partially oxidising haematite would not be fully converted to magnetite, resulting in brown rather than black

Table 1: Comparison of average chemical compositions of black gloss in Early Bronze Age and Attic Pottery. Concentrations expressed as % oxides (Fe as FeO) (Aloupi and Maniatis 1990; Aloupi 1993; Maniatis et al. 1993).

Black gloss	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**K**	**Ca**	**Ti**	**Mn**	**Fe**	**Al/Si**
EBA, Thera	1.4	2.6	22.0	48.7	0.5	0.3	0.1	5.9	4.4	0.5	0.3	18.3	0.45
Late Geometric, Naxos	1.9	2.9	26.9	44.0	0.3	0.2	0.3	6.2	1.9	0.6	0.2	14.7	0.61
Archaic Period, Attic	1.0	2.6	28.9	45.4	0.2	-	0.1	6.1	1.0	0.7	0.1	14.2	0.64
Classical Period, Attic	0.7	1.9	30.3	45.2	0.4	0.1	0.1	5.3	0.6	0.7	0.1	14.9	0.67

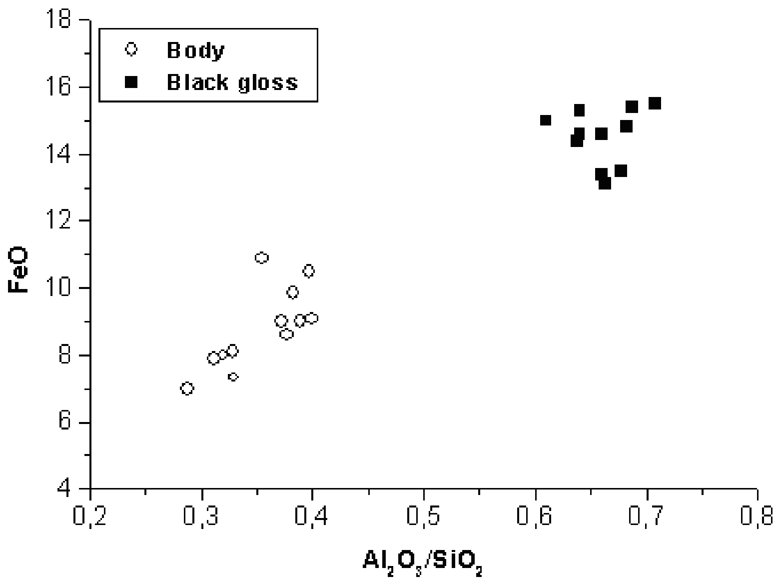

Figure 16: Fe concentration plotted against the ratio Al/Si for the body and the black gloss of a number of Attic pottery of the 6th and 5th century BC.

colours. There are a lot of examples of both cases of failed black gloss in antiquity. The controlled reduction at this stage produces the optimum degree of sintering and vitrification so that the paint layer becomes compact and impermeable to gasses, excluding in this way any diffusion of oxygen into it and prohibiting the re-oxidation of magnetite at the final oxidising stage.

At the third stage, a re-oxidation of the porous body occurs and its colour is reinstated to a great degree to the initial pink/reddish colour of the first stage. However the paint layer is impermeable and cannot be re-oxidised (if the reducing conditions are right, as explained above), remaining black and stable until the end of the firing cycle.

Figure 18 shows approximately the colour changes occurring in the body and paint during the various firing stages for producing a black glossy decoration on a pink or light red body, as that observed on the red-figured or black-figured Attic vases. The surface

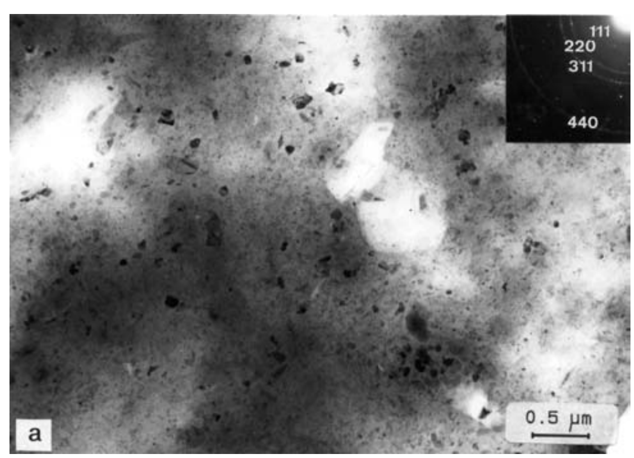

Figure 17: Micromorphology of Attic black gloss under the transmission electron microscope at high magnifications (75,000 x). The black grains are magnetite or hercynite particles, their typical electron diffraction pattern is shown on the top right-hand corner (Maniatis et al. 1993).

of the vessel made of a calcareous clay is wiped with a wet sponge to make the surface smooth. The colour of the raw body clay was almost certainly grey, as all the natural fine calcareous clays that can be found in Greece. The decoration that is going to come out black is painted with the specially refined clay, as discussed earlier. The initial raw colour of the paint material was either orange or red due to its enrichment in iron oxides. The difference in colour of the raw clays between body and paint helped the artist to paint the decoration details, which in some cases were extremely fine. The rest of the surface was not covered with any other slip or material in order to remain porous and facilitate its re-oxidation during the final oxidising firing stage.

In conclusion for the black gloss paint on the Attic vases, the selection and extremely high refinement of the raw materials and the control of the kiln during the complicated three-stage firing is reflecting a very high technology level. It surely denotes an important technological achievement at the end of a progressive development for about 1000 years from the date it was first tried in MBA, about 6000 years after the first appearance of ceramics. This manufacturing know-how in conjunction with the beautiful angiographies gave these vases a very high trading value.

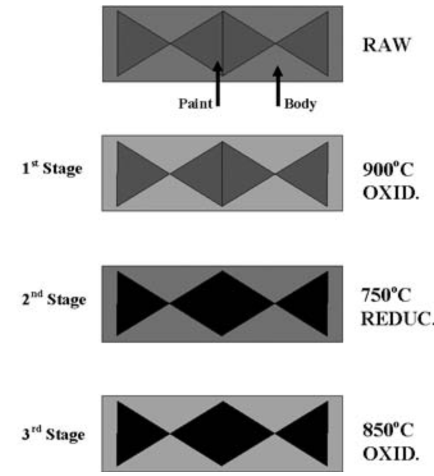

Figure 18: Diagram showing the colour changes during the three-stage firing for the production of the Attic black gloss.

Red gloss in conjunction with black gloss

There are some Attic vessels, although very rare, bearing simultaneously black and red gloss decoration on a pink or light-red body. The term red gloss refers to a red sintered and glossy paint having more or less the same appearance as the black gloss except that it is red in colour. This paint was sometimes called "intentional red glaze" (Farnsworth and Wisely 1958) in order to signify the fact that it was a paint designed to come out of the firing red and glossy, and it is not a failed black gloss or a background red colour. The intentional red gloss should not be confused with the so-called 'accessory red' which is a coarse matt paint of a purple colour. Given the fact that the red gloss paint layer is sintered and may block the entry of oxygen at the last oxidising firing stage, its presence on a ceramic surface together with the black gloss presents a challenging technological achievement and makes its scientific investigation quite interesting.

Some researchers (Richter 1951) had suggested that the paint for the red gloss was applied after the first three-stage firing that produces the black gloss and a second purely oxidising firing was necessary for the red gloss. One of the earliest scientific investigations of the intentional red gloss combined also with reproduction experiments took place in 1958 (Farnsworth and Wisely 1958). They suggested that a second firing was not necessary. The intentional red was made from the same clay used for the black gloss by adding to it some quantity of very fine ochre prepared in a suspension. The added ochre delays sintering and vitrification and thus, both paints were applied on the vessels when the body was in a leather-hard state and a single three-stage firing was performed. During this firing the black sinters and becomes a coherent solid mass as discussed before, while the ochre-containing glaze remains porous and is easily reoxidised at the last oxidising stage. More recent work (Tite et al. 1982) using scanning electron microscopy suggested that addition of ochre to the red gloss cannot be verified by analysis and microscopic examination. However, the more porous texture of the red gloss that would allow reoxidation during the final oxidation firing stage was verified. This according to the authors could be obtained by collecting a fine but slightly coarser fraction from the suspension during the refining process to prepare the black paint. Using these two fractions the black and red gloss can be produced simultaneously in a single three-stage firing.

New analysis and examination of the intentional red gloss on Attic vases of the 6th and 5th century which is under progress at the Laboratory of Archaeometry, NCSR "Demokritos" is providing interesting but a bit puzzling new evidence. The intentional red gloss seems to have at least two versions. The 5th century sample, called also 'coral red' contains a higher amount and particle size

Table 2: Examples of the basic chemistry of various Attic red paints co-existing with black gloss.

Sample	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**K_2O**	**TiO_2**	**FeO**	**Al/Si**
Black Gloss	0.74	1.40	31.14	46.48	4.78	0.49	14.99	0.67
Red Gloss	0.77	1.49	31.62	45.37	4.63	0.55	15.00	0.69
Coral Red	1.77	1.89	27.68	46.29	3.47	1.25	16.88	0.60
Accessory Red (Purple)	-	-	5.88	34.34	2.39	0.56	54.05	0.17

distribution of iron oxides and the degree of refinement of the original clay (Al/Si = 0.60) is less than that of the black gloss (Table 1). This could well have been produced by adding ochre to the paint prepared for the black gloss. It is most probably the type of "intentional red" examined by Fansworth and Wisely (1958), so their suggestion makes sense. On the contrary, our 6th century sample is of a very different nature. The chemistry and microstructure are very similar between black and red (Table 2). This agrees more with the samples examined by Tite et al. (1982), but only as far as the similarity in chemistry between black and red gloss is concerned. As far as the microstructure is concerned, in our case they are identical between black and red (Kavoussanaki 2002). Polished sections of black gloss and red gloss on the same Atttic vessel exhibit the same size and distribution of iron oxide particles and same degree of sintering. This similarity makes it very difficult to understand how the red paint layer could have been re-oxidised but the black could not. One wonders if there are any minute porosity differences, undetectable with the SEM that could perhaps explain the re-oxidation of the red paint at the final firing stage; this has to be proven by further investigation. The possibility of a second firing in oxidising atmosphere just for the red, using exactly the same paint material as for the black, must be excluded, as the optical microscope examination reveals a black zone in the red gloss paint at its innermost side. This black zone is clear evidence that this paint has undergone a reducing cycle at an intermediate stage, the density of which being such that it was not fully re-oxidised, down to the deepest layer close to the vase body, during the final oxidizing stage. A paper presenting these new experimental results is under preparation.

Conclusions

I hope this paper has shown the invaluable contribution of scientific techniques in the study of ancient ceramic technology. This was the result of systematic and dedicated work by several archaeometrists during the last few decades, one of them being undoubtedly M.S. Tite. Important information on various aspects of ceramic technology has been extracted from the moment of its emergence until recent times. We now know the role of clay chemistry and firing properties of the different natural clays and the effect of treatment of the raw materials. We also know that ancient potters progressively understood better and deeper the parameters influencing the physical and chemical properties and quality of the final product. Through the selection of suitable materials, the modulation of their properties by ingenious treatment and clever manipulation of the kiln conditions, the ancient potters reached an extremely high level of ceramic technology in classical times. This was followed by the development of transparent glazes and porcelain. The scientific investigation of ancient ceramic technology has allowed the understanding of the technological solutions adopted in each period and place and has shed light on the techniques used for the production of most known types of ceramics all over the ancient world.

Archaeologists have realised the importance of these new developments and collaborate systematically with archaeological scientists for ancient ceramic technology studies. A number of them are engaged themselves in scientific examination and have acquired experience in reading and interpreting the scientific results. We have gone far beyond the earlier times when archaeologists described the pottery only by body form and style of decoration and the times when they believed the different ceramic colours observed were solely due to different clays used, being totally unaware of the dramatic effects on the colour of the firing temperature and atmosphere.

It is now clear that the full understanding of ancient ceramic technology and its social and economic implications can only be obtained through an integrated approach. This involves the investigation of the system: clay selection and refinement – refractory properties – firing temperature and atmosphere – mechanical and thermal properties – decoration technique – availability and provenance of raw material – social context and use.

There is still a lot to be learned, many different types of ceramics to be investigated but the most important goal has already been achieved. This is the set of unique developed methodologies and background knowledge obtained by the previous archaeometric generation. These are now inherited by the younger researchers of the field and allow the integrated study of any group of ceramics and the assessment of the level of technology and know-how in any period or area.

Note

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Chapter 3

Neolithic pottery from Switzerland: raw materials and manufacturing processes

M. Maggetti[1]

Abstract

The Neolithic pottery found at the twelve Swiss sites investigated so far was predominantly manufactured from silicate, fatty clay. This forms a contrast to the clayey objects which were produced from very local, mainly carbonate clays. The former contains approximately 10–30 vol% temper. The clayey objects, on the other hand, were either non-tempered or tempered with organic substances. Two vertical sections show the local origin of the artificially added, a-plastic elements. The oldest ceramic (appr. 5250 BC) found at Bellinzona-Castelgrande TI, for instance, was tempered with gneiss, whereas ceramic from the intermediate time slot (3750–1800 BC) contains mainly amphibolite. Gneiss is again predominant in the objects from the youngest layers. Ceramic from eleven sites of the Swiss Midland show that, over time, granitoid rock became the temper material of choice. This may be due to its characteristic to crumble into a granulous heap when heated in fire and quenched in water. Many potential temper rocks occur in local moraines, dating from the Riss and Würm glaciations, but the Neolithic potter selected specifically mainly granitoids. Generally, pots were manufactured with coils of clay, which were either spiraled upwards or piled up. Swiss Neolithic pottery was open-fired, either in surface bonfires or in pits. The ceramic body recorded temperatures in the range of approximately 500–700°C. Twenty fragments of eleven crucibles from the Pfyn culture from five Swiss provenances were analyzed in order to understand if they were used as smelting or only as casting crucibles. They were made of local, high CaO- as well as low CaO-clays, and most of them were tempered with threshing waste, i.e. chaff. The uppermost parts of the crucibles are molten, which may be explained by the use of blow-pipes acting upon the crucibles from above. The inner parts of these objects show a significantly higher concentration of copper than do the parts which face away from the blow-pipes. In the scorified areas, mostly chalcopyrite and less frequently copper, cuprite, bornite, and chalcanthite can be found. While the use of casting crucibles seems most plausible, it may be possible that some crucibles were utilized for smelting sulphide ores.

Introduction

The earliest Neolithic settlement in Switzerland is located on the top of mount Bellinzona-Castelgrande (approximately 5250 BC, Stöckli 1995). However, Neolithic settlements in the Swiss Midland were preferably established around lake shores and especially on the lake beaches. On the one hand, no clearing of the area was necessary before a village could be built, on the other, the lakes offered a suitable means of transport. SPM II (1995) provides an excellent representation of current archaeological knowledge of the different Neolithic cultures in Switzerland.

Very few papers summarizing and providing an overview of archaeometric investigations on Neolithic ceramics in Europe have been published so far (e.g. Gibson and Woods 1990; Hardmeyer et al. 1995; Muntoni 2002). While the studies of Hardmeyer et al. (1995) focused on the archeological interpretation of scientific results, the following discussion will be

Table 1: Number of Neolithic pottery samples from Switzerland studied by optical microscopy, X-ray fluorescence (XRF) and X-ray diffraction (XRD). Date according to Cueni et al. (1995) and Stöckli (1995).

			n analyses			
Location	**Cultural group**	**Date (BC)**	**microscopy**	**XRF**	**XRD**	**Literature**
Arbon-Bleiche 3 (AB)	Pfyn / Horgen	3384–3370	163	163	163	Bonzon (2003)
Auvernier-La Saunerie (AS)	Auvernier cordé	ca. 2700	16	16	16	Benghezal (1993, 1994)
Bellinzona-Castelgrande (BC)	Castaneda	2600–2500	15	15	15	Schubert (1986), Zanco et al. (2003)
	Lagozza	3750–3500	16	16	16	"
	Vasi a bocca quadrata	4500–4000	31	31	31	"
	Neolitico inferiore	5300–4500	15	15	15	"
Burgäschi See-Süd, SW and Nord (BS)	Cortaillod classique	3760–3748	60	60		Nungässer and Maggetti (1978, 1981)
Delley-Portalban (DP)	Auvernier cordé	2634–2440	43	43	43	Benghezal (1994b)
	Auvernier cordé	2700–2650	50	50	50	Di Pierro (2002, 2003)
	Auvernier cordé	2634–2440	6			Sturny and Ramseyer (1987)
Egolzwil 3 (E3)	Egolzwil	4282–4275	15	15	15	Schubert (1986, 1987)
Kleiner Hafner, ZH (KH)	spätes Horgen	2802–2781	5	5	5	"
	östliches Horgen	3222–3201	7	7	7	"
	Pfyn		8	8	8	"
	klassisches Cortaillod	3968–3831	27	27	27	"
	frühes Cortaillod	4231–4032	23	23	23	"
	Egolzwil	4384–4280	15	15	15	"
Muntelier-Platzbünden (MP)	Horgen occidental	3179–3118	40	40		Rodot et al. (2003)
St. Blaise-Bains des Dames (SB)	Auvernier cordé	2640–2450	9	9	9	Benghezal (1993, 1994)
	Lüscherz	2794–2673	8	8	8	"
	Horgen occidental	3166–3121	6	6	6	"
	Auvernier cordé	2640–2450	63	63	63	Di Pierro (2002, 2003)
Sutz-Lattrigen Rütte (SL)	Auvernier cordé	2754–2652	30	30	30	Benghezal (1993, 1994)
Twann-Bahnhof (TB)	Horgen	3405–3072	20		20	Nungässer et al. (1985)
	Cortaillod classique	3838–3768	80		80	"
Vinelz-Alte Station (VA)	Auvernier cordé	2793–2715	30	30	30	Benghezal (1993,1994)

based on material-technical aspects, mainly the selection and preparation of raw materials and the firing processes. Table 1 provides a general overview of the 12 sites that were investigated, Figure 1 indicates their location and Table 2 the chronology of the Swiss Neolithic period.

Terminology

It is generally known that in clay-based ceramic objects, non-plastic parts are distinguished from previously plastic parts, i.e. the clay minerals. Non-plastic elements are, according to Maggetti (1979), all grains of an average diameter of ≥ 0.015 mm. In Swiss archaeometrical studies, the differentiation between naturally present and artificially added (temper) a-plastic inclusions is based on the criteria derived by Maggetti (1994), i.e. (1) bimodal (hiatal) distribution of the non-plastic grains; (2) angular outlines of the temper grains; (3) organic material; (4) grog, complemented by the comparison with local raw clays,

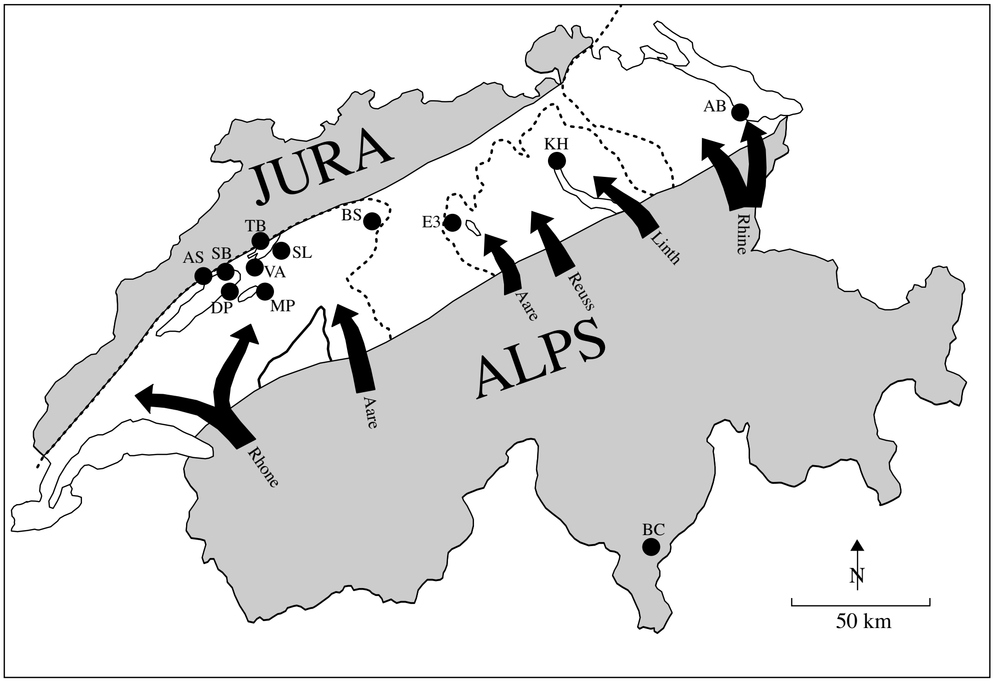

Figure 1: Location of the studied settlements. Dashed line = boundaries of the glacier dating from the Würm period. Arrows = direction of movement of the Würm glaciers. Abbreviations see Table 1.

BC	Svizzera meridionale	Wallis/Valais	Suisse occidentale	Zentralschweiz	Ostschweiz	BC
2000	Bronzo antico	Bronze ancien	Bronze ancien	Frühbronzezeit	Frühbronzezeit	2000
		Campaniforme	Campaniforme	Glockenbecher	Glockenbecher	
2500	Castaneda	Néolithique final valaisan	Auvernier cordé	Schnurkeramik	Schnurkeramik	2500
			Lüscherz	spätes Horgen	spätes Horgen	
3000	Carasso-Tamins		Horgen occidental	östliches Horgen	östliches Horgen	3000
			Port-Conty			
3500		Cortaillod-Saint-Léonard	Cortaillod tardif	spätes zentralschweiz. Cortaillod / zentralschweiz.	spätes Pfyn	3500
	Lagozza	Cortaillod-Petit-Chasseur	Cortaillod classique	klass. Zentralschweiz.	Pfyn	
4000		Cortaillod ancien valaisan	Cortaillod ancien	Frühes zentralschweizerisches Cortaillod	Lutzengüetle	4000
	Vasi a bocca quadrata			Egolzwil	spätes Rössen	
4500		Néolithique ancien valaisan	Précortaillod	Frühneolithikum	Rössen	4500
					Grossgartach	
5000	Neolithico inferiore padano-alpino		Néolithique ancien (La Hoguette)		Bandkeramik	5000
5500						5500

Table 2: Time line of the Swiss Neolithic Cultures (Stöckli 1995). Empty spaces represent gaps in the scientific knowledge, not interruptions of the occupation.

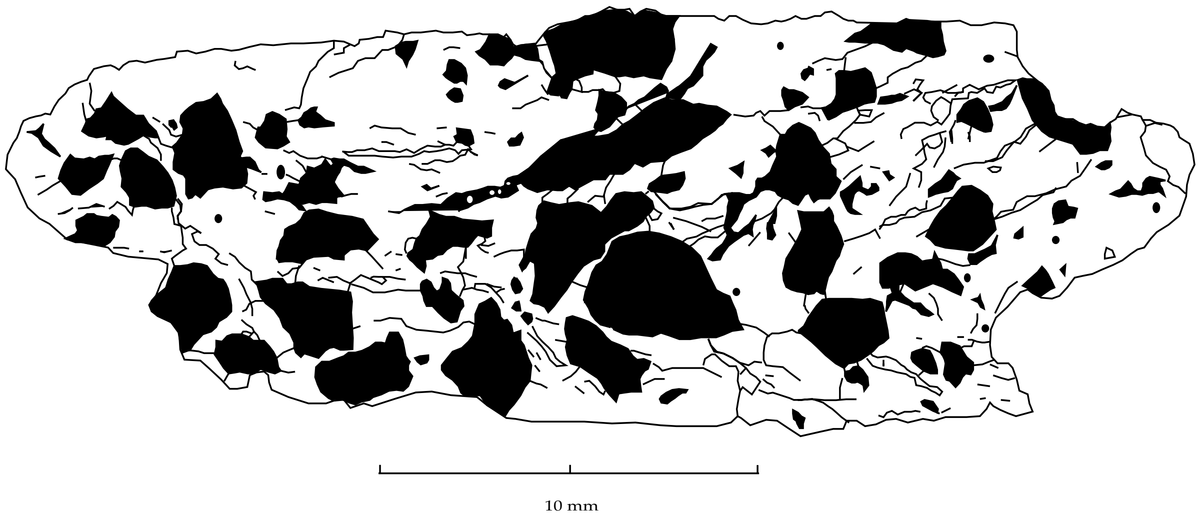

Figure 2: Coarsely tempered Neolithic ceramic, with temper in black.

whereby grains of a diameter ≥ 0.5 mm (Benghezal 1994; Bonzon 2003) or ≥ 1 mm (Di Pierro 2002) indicate artificially added temper. Figure 2 is a typical example of a coarsely tempered Neolithic ceramic, showing hiatal distribution of the added, angular granitic fragments. The matrix is defined as the clay used for the pottery production and contains therefore previously plastic components, as well as non-plastic elements ≤ 0.5 mm and ≤ 1 mm respectively. A fatty matrix is inclusion-poor (0–5 vol%), a meager matrix inclusion-rich (> 5 vol%). A silicate matrix contains predominantly silicate minerals, a carbonatic matrix mainly carbonate minerals and a silicatic-carbonatic matrix consists of silicates and carbonates in equal proportions.

Geology

The investigated sites are located in the Swiss Midland, situated between the Jura Mountain belt and in the Alps (Bellinzona-Castelgrande) (Fig. 1). The Tertiary basement (Oligocene to Miocene) comprises predominantly sandstones and marls and is covered by Quaternary moraine deposits, composed mainly of Pleistocene sediments from the Riss and Würm glaciations. They consist of ground moraine clays, sands, coarse pebbles and big erratic boulders. During the Holocene, clayey, silty, and sandy sediments were deposited in lakes and ponds, which formed as a result of glacial retraction.

Clays for the pottery production

Unfortunately, a detailed description of the matrix is not available for all samples discussed here. However, the 601 sherds (Table 3) can provide an indication as to the selection of clay. Even though the number of different matrix-types varies between the sites, the overall conclusion can be reached that Neolithic

Table 3: Number of pottery samples belonging to the different matrix types.

Settlement	Meager Silicate	Sil. Carb.	Carb.	Fatty Silicate	Sil. Carb.	Carb.	Hetero-geneous	Total
Arbon-Bleiche 3	5	-	6	152	-	-	-	163
Auvernier-La Saunerie	3	3	1	3	4	-	-	14
Burgäschi See-Süd, SW and Nord	-	-	-	58	-	1	1	60
Delley-Portalban	34	3	-	30	23	2	4	96
St.Blaise-Bains des Dames	14	4	6	26	56	3	-	109
Sutz-Lattrigen Rütte	15	1	1	6	4	3	-	30
Twann-Bahnhof (Cortaillod)	37	-	-	26	-	17	-	80
Twann-Bahnhof (Horgen)	8	-	-	12	-	-	-	20
Vinelz-Alte Station	10	1	5	7	6	-	-	29

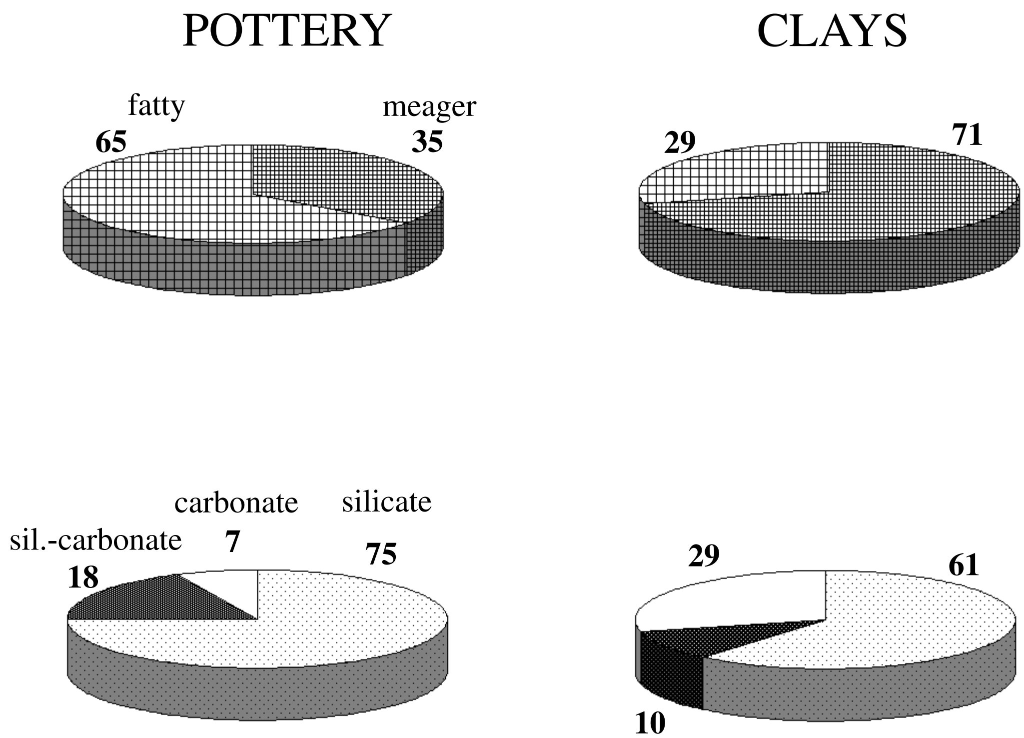

Figure 3: Percental distribution of the different matrix-types in Swiss Neolithic pottery (n=601) and of clays (n= 41) from Western Switzerland (Benghezal 1994).

potters preferred fatty, silicate clay (Fig. 3). So, what types of clay were available to the artisans in those days? When studying 41 superficially outcropping raw materials taken from the vicinity of the investigation sites in Western Switzerland, Benghezal (1994) observed predominantly meager silicate clay (Fig. 3).

The studies of Sigg et al. (1986) have shown that the CaO-content in the Holocene lake sediments are subject to large fluctuations, vertically as well as horizontally. According to detailed studies by Gasser and Nabholz (1969), Jenny and de Quervain (1960, 1961), Mumenthaler (1979) and Peters (1961), the Pleistocene, fine grained sediments found in the Swiss Midland are characterized by a high carbonate content of 25–50 wt%. In fact, it is a common propriety of a carbonate-rich, clayey sediment to be carbonate-poor to carbonate-free in the top layers. This is due to the original carbonate minerals having dissolved in acidic ground water and then precipitated again at deeper layers. This could explain why the ceramics have less carbonate matrices (25% of 601 matrices) in comparison to the clay matrices (39% of 41 matrices). However, the discrepancy between the dominantly fatty matrices in the Neolithic pottery and the meager matrices in local raw materials suggests clearly that Neolithic potters consciously selected fatty, silicate clay. On the one hand, this type of clay can be moulded easily because of its high plasticity, on the other hand, it can be fired without difficulty due to the absence of carbonate. This applies to open firing in particular, as here temperature cannot be controlled and firing temperatures fall within the critical range for post-firing spalling, i.e. 600–800°C. Another possible explanation could be that Neolithic potters refined meager clays by soaking. However, this is contradicted by the experiments of Di Pierro (2002), who proved that local, soaked clay is not chemically compatible with the separated matrices (see below). But, do these clays occur locally? None of the previous studies has provided convincing evidence of the use of local clays, i.e. raw material found within 1–2 km (Arnold 2001), in Neolithic ceramic production. As a result, Di Pierro (2002, 2003), continuing preliminary experiments of Benghezal (1994b) and Marro (1978), developed a method which allows the matrix to be separated from the temper in low fired sherds. This process was tested on samples from the sites of Delley-Portalban (n=17) and St. Blaise-Bains des Dames (n=17). Both productions could be distinguished clearly (Fig. 4), with the exception of some samples

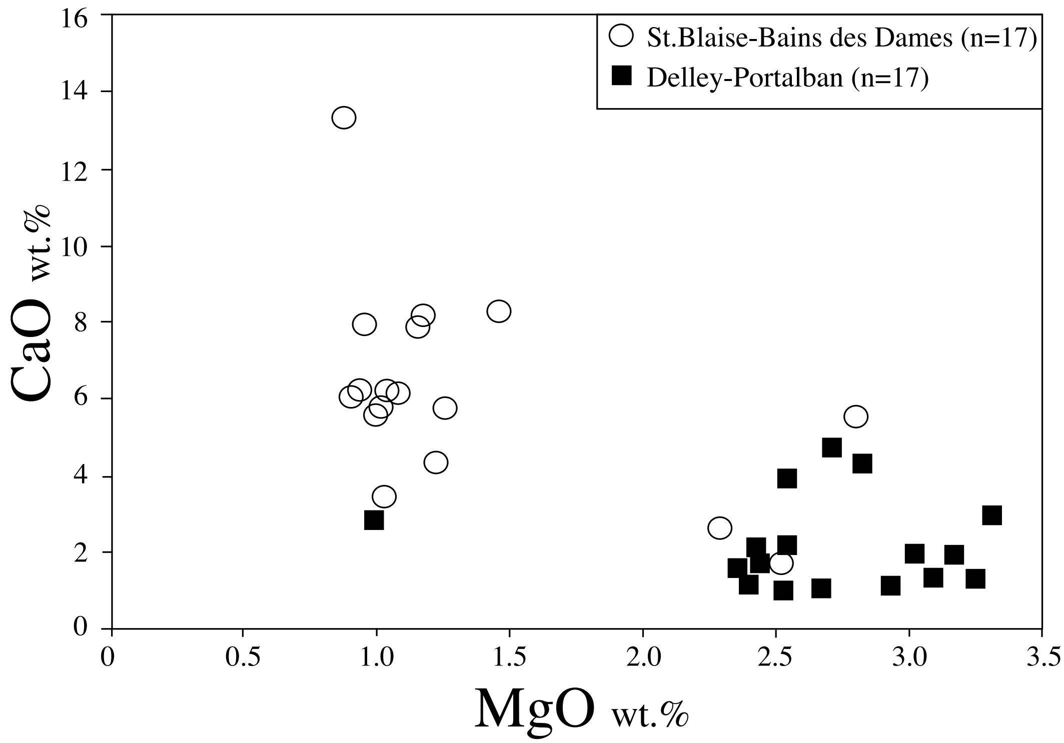

Figure 4: CaO-MgO plot of the matrices of Delley-Portalban and St. Blaise-Bains des Dames pottery (Di Pierro 2002).

which have been discussed in detail by Di Pierro (2002). The matrices from St. Blaise have generally a lower MgO- and a higher CaO-content and the considerable fluctuation in CaO can be attributed to the proximity of the Jura Mountain belt, rich in limestones and marls. This indicates the use of two different clays and, as a result, local production is more likely than production in one centre. Despite this new method, no adequate raw material could be identified in the close neighbourhood of the studied sites, which can be explained (1) by the fact that the prospecting was insufficient, i.e. that the Neolithic clay pits were not detected; (2) by the fact that the clays have been completely used by the Neolithic potters; and (3) that the clay areas have been completely built over. However, this new separation technique represents a promising tool for the future.

Temper for the pottery production

The authors of the publications discussed here postulate either a local or regional production for most of the examined objects. Only a few pieces have been identified as imports. These would have been introduced from an area of no more than 20 km away (Schubert 1987). The following discussion examines, based on the tempered pieces, whether the petrographic nature of the temper changed over time and within certain cultures. Two vertical examples – Castelgrande, Bellinzona (appr. 4'000 years of settlement) and Kleiner Hafner, Zurich (appr. 1'800 years of settlement) as well as four horizontal time slots have been selected for this purpose.

Vertical sections

Bellinzona-Castelgrande (Ticino): The pottery found during the Bellinzona-Castelgrande excavations by P. Donati (1980 – 1984) provides a unique insight into European Prehistory (Carazzetti 1986, 1993; Carazzetti and Donati 1990). Typological classification by R. Carazzetti shows that the ware represents a complete sequence from the early Neolithic (± 5300 BC) to the Late Bronze Age (± 1200 BC), suggesting a permanent settlement of the area around Bellinzona for about 4'000 years (Fig. 5). In addition, some objects belonging to the Early Iron Age (700–600 BC) were found, giving the opportunity to study the time-related development of pottery technology and changes in the used raw materials. 111 samples of different typologies and ages (77 Neolithic ceramics, Table 1) were analyzed, including samples from the Bronze (n=18) and Iron Ages (n=16).

On the basis of the petrographic nature of the non-plastic inclusions, Zanco et al. (2003) identified two

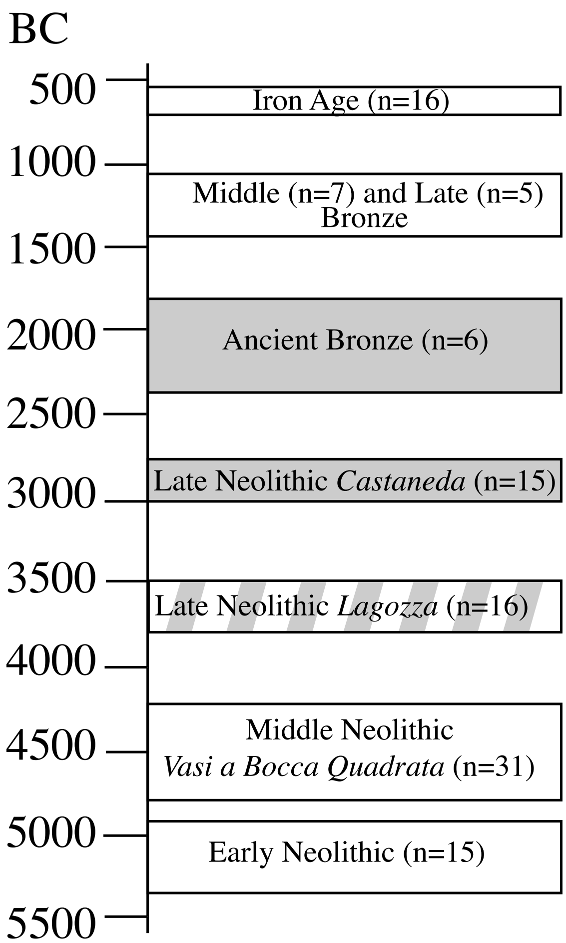

Figure 5: Vertical section of the human occupation at Castelgrande, Bellinzona. Shaded = prevailing amphibolitic temper. White = prevailing gneissic temper.

main petrographic groups: (1) in the first (gneissic type) many gneissic and granitic fragments were recognized, with minor amounts of micaschists and quartzites. Quartz, feldspars, muscovite and sometimes biotite represent single crystals distributed in the groundmass; (2) the second group (amphibolitic type) comprises ceramics characterized by amphibolitic fragments in addition to quartz, muscovite and feldspars monocrystals.

In the course of the 4'000 production years, a remarkable change in the specific choice of the temper material took place (Fig. 5): (1) approximately 5500–3500 BC: the ware of the Neolitico inferiore padano-alpino (Early Neolithic), Vasi a Bocca Quadrata (Middle Neolithic) and some fine Lagozza (Late Neolithic) belongs to the gneissic petrographic type; (2) 3750–1800 BC: from coarse Lagozza to Bronzo antico (Ancient Bronze) the ceramic products are characterized by amphibolitic inclusions; (3)

Table 4: Amount of Verrucano temper (vol. %) in the Neolithic station of Kleiner Hafner, ZH (Schubert 1986, 1987)

Culture	**n**	**Verrucano**	**Rest**
Spätes Horgen	5	100	-
Östliches Horgen	7	43	57
Pfyn	8	87	13
Klass. Cortaillod	27	96	4
Frühes Cortaillod	13	46	54
Egolzwil	15	60	40

1400–1100 BC: from the Middle Bronze to the Late Bronze, the potters go back to produce pottery with a gneissic type of temper. The same kind of temper belongs to the Iron Age pottery.

Kleiner Hafner, Zürich: The ceramics date from 4500 to 2700 BC, i.e. come from a period of 1'800 years. The temper typically used by nearly all cultural groups consists of coarse grained and fine grained verrucano-fragments, i.e. a deformed and metamorphosed quartz porphyry (Table 4). The ceramics belonging to the oldest Egolzwil cultural group (4384–4280 BC) are of heterogeneous composition in regards to their a-plastic inclusions. According to Schubert (1987), verrucano, sandstone, radiolarite, quartzite, mica schist and granite are present. Half of the 15 analyzed samples show a hiatal distribution of the non-plastic elements, which suggests tempering. In the following group, that of the older Cortaillod, i.e. "frühes zentralschweizerisches Cortaillod" of Table 2, (4231–4032 BC), the pottery does not differ significantly from the previous group and the non-plastic constituents present are markedly heterogeneous. Coarse a-plastic inclusions are interpreted by Schubert as temper. However, some pots belonging to this culture were tempered with fossil fragments (19–29 vol%) as well as granite. Furthermore, these pots stand out due to a high total temper-content (26–37 vol%). Palaeontological investigation reveals Mesozoic (Oxfordian/Dogger) fauna of the Jura Mountains, which are located at a distance of 20 km from the Kleine Hafner area. This type of ware may therefore have been imported. In the younger Cortaillod group, i.e. "klassisches zentralschweizerisches Cortaillod" of Table 2 (3968–3831 BC), verrucano is the dominant temper material, an indication of a systematic selection of this material. The Pfyn-ceramic resembles the previous pottery in terms of a-plastic constituents. Granitic fragments are the main constituents of the temper of the older Horgen, i.e. "östliches Horgen" of Table 2 (3222–3201 BC) ceramic. The temper of the

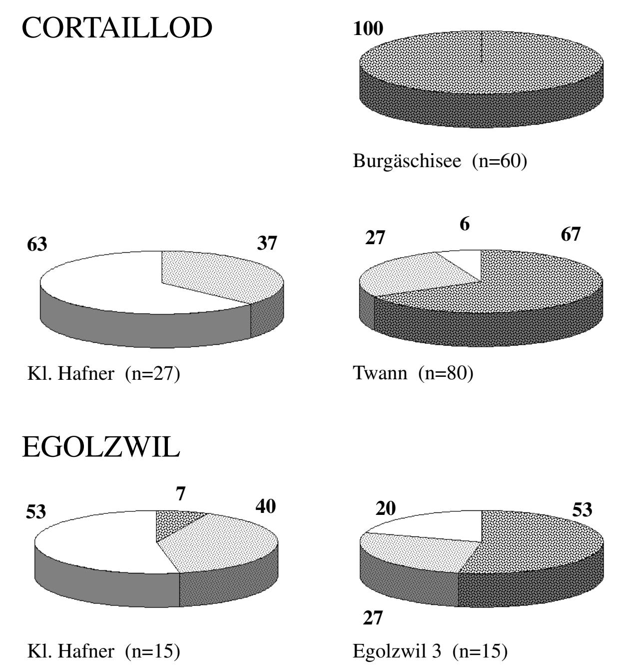

Figure 6: Percental distribution of the three temper types in pottery of the Egolzwil and Cortaillod cultures (dark shaded area: granite only, light shaded area: granite with other rocks, white area: no granite).

younger Horgen, i.e. "spätes Horgen" of Table 2 (2802–2781 BC), on the other hand, is more varied (sandstone, quartzite, verrucano).

Horizontal (culture) time slots

Egolzwil (4500–4000 BC): A noticeable feature of nearly all sherds collected at the site of Egolzwil 3 is a coarse, most often granitic temper, which was added to a very fatty, silicate clay. An unusual characteristic is the presence of angular grog fragments, with a considerable part of the total sherd volume of up to 9 vol%. This forms a contrast to the ceramic of the Kleiner Hafner, which is of the same age and where such a temper is absent. The latter is of a very heterogeneous composition and characterized by verrucano fragments, which are missing from the Egolzwil 3 ceramic. Both products can therefore be well differentiated. Another petrographic criterion can be used too, as the Egolzwil 3 pottery contains much more granitic temper than the Kleiner Hafner products (Fig. 6).

Cortaillod (4000–3750 BC): While granitic temper is most common at the sites of Western Switzerland (Fig. 6), its (quantitative) occurrence decreases in the region of lake Zurich, where verrucano is dominant (Table 4).

Classic Horgen (3500–3000 BC): The ceramic of the transitional period between Pfyn/Horgen found at Arbon-Bleiche 3 contains generally, but not exclusively, a granitic temper (Fig. 7). Its amount increases in the pottery of the Swiss Neolithic stations going from East to West.

Auvernier cordé (2700–2500 BC): The ceramic of all sites was mainly tempered with granite (Fig. 7). Fossil-rich pottery is interpreted as an import from the Jurassic realm.

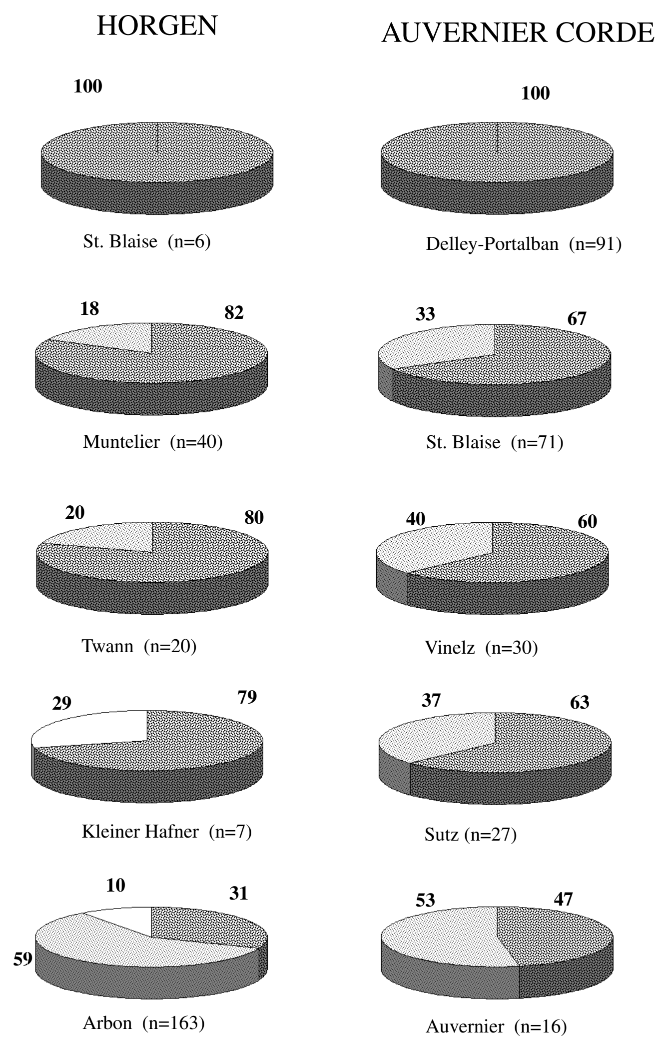

Figure 7: Percental distribution of the three temper types in pottery of the Auvernier cordé and Horgen cultures (dark shaded area: granite only, light shaded area: granite with other rocks, white area: no granite).

Interpretation

Bellinzona-Castelgrande: This settlement was located on a mount consisting of interbedded strata of gneiss and amphibolite. The temper material was therefore right on the potters' doorstep, so to speak. The evolvement of temper, as in the case of Bellinzona-Castelgrande, is puzzling and difficult to explain. Technical reasons seem not plausible enough, so socio-cultural aspects are probably the motivation. Only comparisons with other, not yet studied Neolithic settlements in Northern Italy will perhaps give an answer.

Midland settlements: The results presented here show that (1) each site of the Swiss Midland is characterized in regards to the petrographic nature of the temper-elements (e.g. verrucano at the Kleiner Hafner) and (2) an evolution to the preferential use of a specific temper, i.e. granitic fragments can be clearly observed, at least in Western Switzerland. However, it needs to be pointed out that, on the one hand, the number of samples is not always statistically sufficient, even when representative samples were taken. On the other, the Central and Eastern parts of Switzerland have been insufficiently investigated.

Potters collected temper material from local moraines. These show a very heterogeneous composition of the sand (Gasser and Nabholz 1969; Jenny and de Quervain 1960, 1961) and boulder fractions. The occurrence of pure granitic sands at all sites would therefore be hard to explain by geological processes only, in view of the fact that the glacial debris represents a collection of a lot of rock types, outcropping in the Alps and the Midland (Fig. 1). Besides, the angular outlines of the granitic temper further contradict the use of a pure natural granitic sand, as latter would show rounded forms. The assumption of a selective enrichment of granitic sand grains by the potter can be discarded as unrealistic, especially in light of the preparation time involved. It can therefore only be assumed that potters added crushed granite to the ceramic mass. However, as shown by Di Pierro (2002) for Delley-Portalban, granitoids make up only 10% of the bolder spectrum of the local moraines. From this, he concluded correctly, that Neolithic potters selected these rocks consciously and specifically. This view has been supported by Di Pierro and Martineau (2002) and Rodot et al. (2003).

For what reason did Neolithic potters prefer granitic rocks? Probably because this type of rock could be treated in order to meet the desired temper fraction by investing a reasonable amount of time and energy. The potters had fire and water at their disposal. Hard rocks when heated in fire and quenched with water, will be softened and afterwards crushed easily by mechanical means. Nungässer et al. (1992) have experimentally demonstrated the efficiency of a high temperature/water-shock treatment for metamorphic granites, i.e. gneisses. This method is essentially based on the following processes: (1) heating (in a bonfire during the experiments) causes a volume increase in the rock. This will be reversed through contraction of those surface areas which have been exposed to the cooling water, eventually causing the creation of very fine cracks; (2) the shift from liquid to the gaseous state for the water which infiltrated these cracks can support further formation of cracks/fissures due to the developing gas pressure; (3) areas of mechanical weakness, such as pre-firing cracks or planar layers of micas in parallel-textured rocks (e.g. gneisses), can also be infiltrated by water and become weakened in their local cohesion. This thermal shock method, a basic as well as efficient process, may therefore have guided Neolithic potters in the selection of suitable boulders.

Production of the pottery

As indicated previously, Neolithic potters preferred fatty silicate clay to which they added up to 40 vol% of temper (average of all analyses: 10–30 vol%). According to Hardmeyer et al. (1995), pots were generally manufactured with coils, which were either spiraled upwards or piled up. Big pots were manufactured in several stages. The pots were then open fired, either in a pit or on surface bonfires. According to Rye (1981), the ceramic body becomes cohesive at lower firing temperatures through dry sintering. This occurs between 400–850°C, depending on the composition of the clay mixture. The minimum temperature required for producing a lasting, water resistant sherd during a short firing period, as is the case in such an open firing, is approximately 550°C (Cardew 1970; Rice 1987; Rye 1981; Tobert 1984). Diffractometric analyses indicate that these temperatures have been reached, hence the ceramic body of the analyzed Neolithic pottery documents temperatures of 500–700°C. These values support ethnological studies of similar fired ware (e.g. Shepard 1954; Wotzka 1991) and experimental findings (e.g. Gosselain 1992; Gosselain and Livingstone Smith 1995). Firing of this kind occurred rapidly, within a period of 30 to 60 minutes (Gibson and Woods 1990). During the extended burial period of the broken pots, the partially destroyed clay minerals can be regenerated (Maggetti 1982). Under such uncontrolled firing

conditions, a fluctuation of the reduction factor is to be expected, i.e. the ratio FeO/FeO_{tot} (Maggetti et al. 1988) will vary considerably (in the studied samples approximately in the range of 0.5–0.7). Most of the reduction factors lie above 0.2, thus documenting a reducing firing atmosphere (Maggetti et al. 1988).

Clayey materials

No relicts pertaining to the production of Neolithic pottery, such as firing waste, have been preserved to serve as local reference material. To overcome this problem, scientists will analyze unfired clayey material for which a local origin is highly likely. This applies to wall plaster (i.e. cobs), plaster coat and loom weights. Cobs are clays used as building material (i.e. clay wall fillings). Plaster coats are crude clay or loam packages for the hearth fire or for clay floors. All these types can be ceramized only involuntarily, e.g. during a destructive fire of a Neolithic village. Loom weights are compacted clay pieces used to pull down animal furs during air

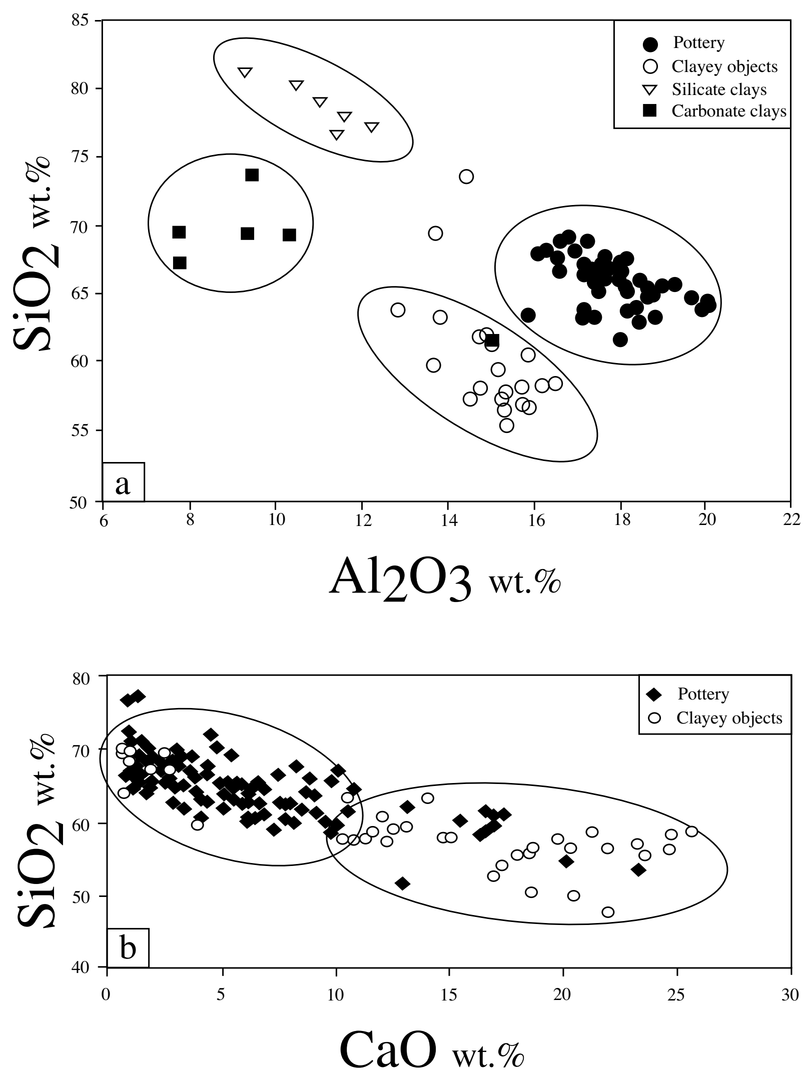

Figure 8 a) SiO_2-Al_2O_3 plot of potteries (n=50), clayey objects (n=21) and local clays (n=12) from Delley-Portalban (Di Pierro 2002). The carbonate clay in the field of the clayey objects is compatible in its overall chemical composition with the clayey objects. It was collected just outside the ancient Neolithic village, proving that these clayey objects are truly local. b) SiO_2-CaO plot (Di Pierro 2002) of 147 potteries and 39 clayey objects from the five settlements studied by Benghezal (1994).

drying. Most of the archaeological literature agrees that they were fired before use. Under the microscope, these clayey objects are very heterogeneous in their structure, the petrographical nature of the a-plastics as well as the granulometry. There is no evidence of tempering, except for the loom weights, where up to 10–15 vol% (Di Pierro 2003) of organic matter was added (Benghezal 1994).

As shown by the settlement of Portalban, all these clayey objects, which were manufactured from local clay, differ significantly from the pottery (Di Pierro 2002) (Fig. 8a). This is supported by a regional perspective (Fig. 8b), which highlights the fact that most clayey objects are considerably CaO-richer than the majority of the pottery. In Western Switzerland, fatty, siliceous clay was used in the production of pots during the Neolithic period, whereas unfired or lightly fired clayey objects were manufactured from siliceous-calcareous to calcareous clay.

Crucibles

Ceramic crucibles are characteristic of the Neolithic Pfyn culture of Eastern Switzerland (Fasnacht 1995) and were studied by Maggetti et al. (1991). A similar object of the Cortaillod culture in Western Switzerland has been characterized with non-destructive methods only (Maggetti and Gloor 1978).

Raw Materials

The eleven analyzed Pfyn objects from five different places are made from a fine-grained, mostly silicate clay. The grain diameter of the largest a-plastic grain never exceeds 0.4 mm. The non-plastic elements consist of fragments of dominating quartz as well as little feldspar and chlorite. Only two possess a carbonate-silicate matrix and thus document the making from a marly clay. The non-plastic amount lies in the range of 15–20 vol%. Rough temper (with a grain diameter of granitic rock fragments up to 3mm) can be observed in five specimens. Longish, spiky pores are found in the objects with fine-grained a-plastics, which are attributable to the presence of now burnt-out, purposely added organic material. Marks of such vegetable fragments are also found on the outside and inside of the crucibles. The spectrum of form and shape corresponds entirely to the description by Schlichtherle and Rottländer (1982), according to which they are fragments of straw, spelts and spindles from ears of corn as well as cereal grains. The proportion of added chaff varies considerably from specimen to specimen. It would appear that temperature resistance of these crucibles was increased by varying the artificially added type of non-plastic elements: (1) organic temper would cause high porosity upon firing; (2) a temper made up of rough fragments of granitoids and gneisses traditionally used in domestic ceramic production would improve the drying and firing properties. Petrographic analysis has shown that at least two clays (silicate, carbonate) were used and that temper was added in order to increase stability. The Neolithic artisans thus did not make a conscious choice of the raw clays, which is also documented by the chemical inhomogeneity of the samples.

Casting or melting crucibles?

Most of the crucibles analyzed show the effects of HT-processes in the form of swollen, melted and pumice-like areas. In most cases, these are only present at the highest parts of the crucibles. However, in a few cases, many can be found on the bottom of the inside or on the handle. As only the uppermost parts of nearly all the crucibles have been affected by the melting phenomenon, heat must have acted upon the objects from above and produced temperatures of over 1100°C, in order to melt the ceramics. X-ray diffraction analyses are consistent with such a punctual high firing, which was caused by blow-pipes acting upon the crucibles from above.

All objects show a polyphase temperature history. The first occurred during the ceramic firing in the T-interval as for the household pottery (500 – 600°C), overlaid by a second HT-phase during metallurgic activities. The inner areas of the crucibles show a significantly higher copper concentration (up to almost 1 wt%) than do the parts which face away from the blow-pipes. In the scorified areas mostly chalcopyrite (Cu_5FeS_2), copper (Cu), cuprite (Cu_2O), bornite ($CuFeS_4$) and chalcanthite ($CuSO_4 \cdot 5H_2O$) were found. Much has been published concerning the form and function of metallurgical objects (melting versus casting crucibles, e.g. Tylecote 1976). The frequently occurring handles and the low capacity would speak for such use of the Pfyn crucibles. Mineralogical and chemical analyses of the studied eleven samples would fit well into this pattern: raw copper, mixed with charcoal which had been stacked on top of it, was melted in the crucible, whereby temperatures above 1100°C were reached by using one or more blow-pipes, which acted on the smelting charge from above and caused the raw copper as well as the ceramics to melt.

On the other hand, Zwicker et al. (1985) have shown in experiments that crucibles of similar size with a capacity of approximately 1 kg may also have been used for the roasting or smelting of copper from sulphide ores. The remains of chalcopyrite would

indicate such use, however, the possibility cannot be ruled out that this formed from copper through retrograde, bacterial processes during the time they were buried in the soil.

The existence of copper mining in Switzerland has been demonstrated for the Early Bronze Age; however, there is no evidence of such an activity during the Neolithic period (Fasnacht 1995). It may therefore be assumed that the copper melted in Pfyner crucibles was very pure (Fasnacht 1991), and it may have come from the Balkan or the Eastern Alps, where copper had already been mined actively since the 5th millennium BC.

Conclusion

This overview of archaeometric papers on Swiss Neolithic ceramic published so far highlights the following points:

1) Neolithic potters consciously selected two different types of clay, depending on the intended use: a fatty, silicate clay for pottery and a meager, carbonate clay for clayey objects. The latter remained before use non-fired or weakly fired. Potters were very aware that calcareous clays needed to be avoided in uncontrollable open firing (where carbonate-critical temperatures of 700–800°C are reached), due to the decomposition of carbonate and the post-firing rehydration of CaO, causing spalling. However, these types of clay were suitable for use as floor lining, wall plaster or loom weights.
2) At present, local provenance has been determined for carbonate, but not for silicate clays.
3) Neolithic potters specifically selected granitic moraine material to use as temper, possibly because such material could be softened and crushed quickly thanks to a fire/water-shock treatment.
4) In Western Switzerland, the use of granitic temper increases progressively from the oldest to the youngest cultural groups. This observation is further corroborated by regional comparisons. This does not apply for the settlement belonging to the Alpine realm, where probably socio-cultural motivations caused a change in temper selection.
5) The firing temperatures of appr. 500–700°C, documented by radiographic means as well as the reduction factors, correspond to the conditions of open firing, either in pits or surface bonfires.
6) Clay was used randomly in the production of the Pfyn crucibles. However, chaff was added purposely, because it causes the formation of longish pores during ceramic firing, which block the propagation of cracks, induced by subsequent metallurgical processes.

The standard of pottery during the Neolithic period was advanced. Potters knew very well how to adapt the local clay and temper spectrum to different applications. Further regional comparisons, particularly in Central, Eastern and Southern Switzerland, will complement and refine the results discussed here.

Note

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Low-tech in Amalfi: provenance and date assignation of medieval Middle-Eastern pottery by application of eyeball technique

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Abstract

A group of glazed pottery fragments used as tesserae was brought to my attention by Jill Caskey of the University of Toronto. It has long been known that these are pieces of 'Islamic pottery' and she asked my opinion of them based on my analytical and typological research on medieval pottery from the Middle East. There are apparently no stray pieces anywhere, so the scientific equipment that can be applied to the problem of provenancing and dating these tesserae essentially comprises my own eye-ball, with assistance only from a 10x hand-lens. An important, indeed key aspect of my research into the provenance and technology of pottery from the Islamic world has been the application of the analytical findings to the typology of the pottery. Typology is quite often defined by technology, i.e. which type of body, glaze, or decoration will be what makes one type different from another, and these attributes will often have geographic and chronological specificity. Similarly it has been an objective in my research to link the provenance information to typological and stylistic attributes in order to relate the data to a much larger group than could be reasonably sampled.

Introduction

In the centuries following the fall of the Roman Empire, a number of small towns flourished in the small bays and hills of the Amalfi coast of Italy. Foremost amongst these is, of course, Amalfi itself, but another important town is Ravello (Fig. 1). An expression of the wealth of this region in this more pious time is found in the churches, in their very construction, but also in the decorations within them, such as wall-paintings and mosaics. A focus for decoration was often the elevated stands used to address the congregation. The earliest of these is the ambo, a platform with two flights of steps, which were first introduced into churches during the fourth century, were in universal use by the ninth, reaching their full development in the twelfth, and then gradually fell out of use, until the introduction of pulpits with single flights of steps beginning in Italy in the 13th century (Catholic Encyclopedia). Along the Amalfi coast these are generally made of marble, and are decorated with mosaics. The tesserae for these mosaics are often coloured stone, or glass, but in some instances the materials used are actually fragments of glazed pottery vessels from the Middle East, from the Islamic world.

These tesserae were brought to my attention by Jill Caskey of the University of Toronto. It has long been known that these are pieces of 'Islamic pottery' and she asked my opinion of them based on my analytical and typological research on medieval pottery from the Middle East. They are pretty well stuck in the mosaic still, and there are apparently no stray pieces anywhere, so the scientific equipment that can be applied to the problem of provenancing and dating these tesserae essentially comprises my own eye-ball, with assistance only from a 10x hand-lens. However, this is exactly the sort of thing I would hope to be capable of. An important, indeed key aspect of my research into the provenance and technology of pottery from the Islamic world has been the applica-

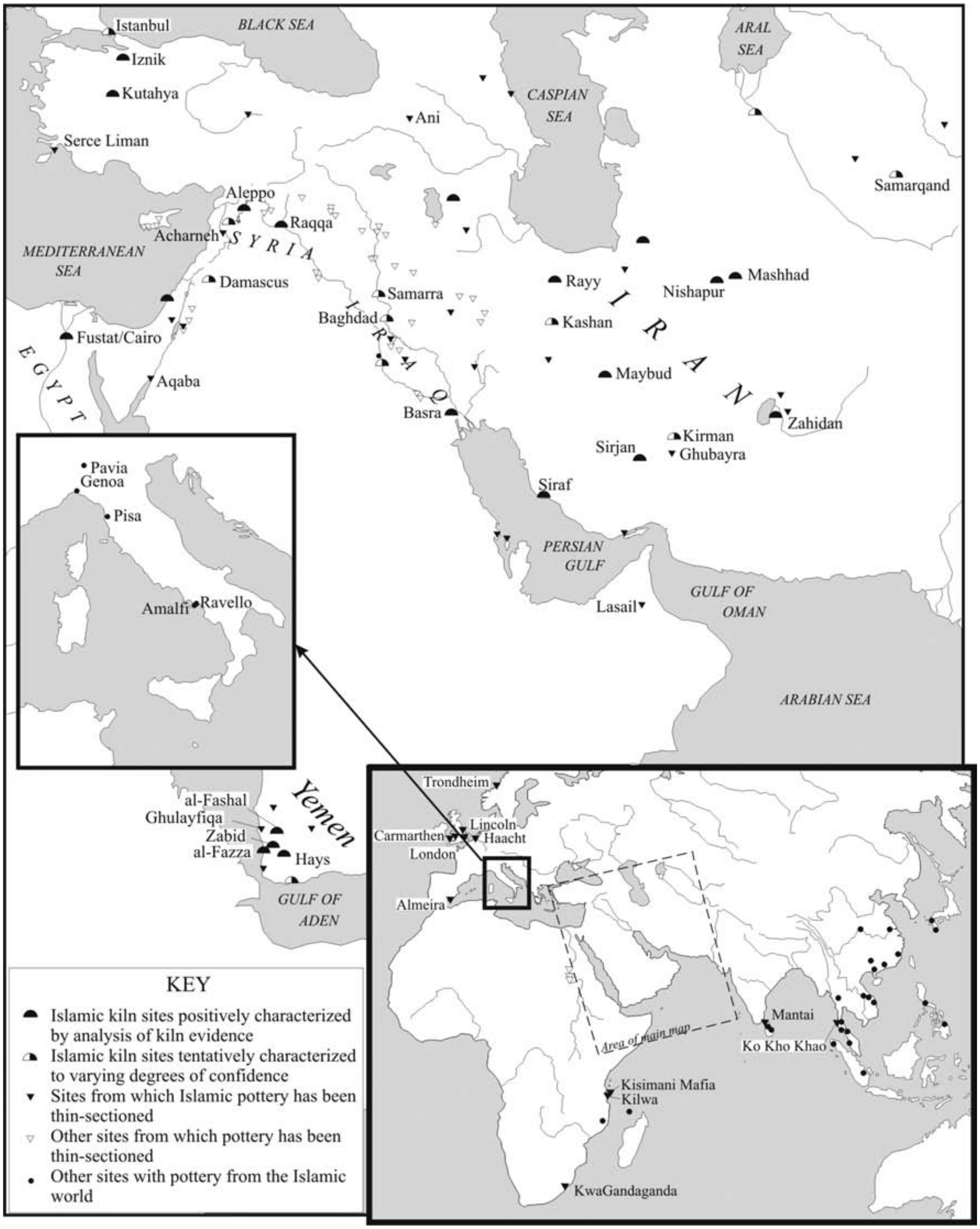


Figure 1: Location Map

tion of the analytical findings to the typology of the pottery. Typology is quite often defined by technology, i.e. which type of body, glaze, or decoration will be what makes one type different from another, and these attributes will often have geographic and chronological specificity. Similarly it has been an objective in my research to link the provenance information to typological and stylistic attributes in order to relate the data to a much larger group than could be reasonably sampled.

So it should be possible to simply assess the attributes of the tesserae and link them to the data from my research (most comprehensively presented in Mason 2004), and determine where the vessels that

were broken up to make these tesserae were made.

Although tesserae and larger fragments can be located in a number of churches in the region, this paper will focus on two particular assemblages, both in Ravello: the ambo of the Duomo or cathedral dedicated to San Pantaleone, and the pulpit of the church of San Giovanni del Toro.

Ravello Duomo

The ambo of the Duomo of San Pantaleone is of typical form with two flights of stairs, made of marble spolia (Fig. 2). The tesserae of pottery fragments are used in mosaics to decorate various parts of the construction, particularly in two figural representations of Jonah being swallowed by the whale. Close inspection reveals two main types of ceramics, lustre-wares and monochrome-glazed wares.

Lustre-wares

The technique of lustre-painting has its origins in glass manufacturing in the centuries before Islam in Egypt and probably also Syria. A traditional description of initial pigment is a mixture of silver and copper in the form of sulphides, nitrates or chlorides, which are finely ground with an ochrous granular clay medium, liquefied by vinegar with gum-arabic or sugar-water to make the pigment flow more easily (Caiger-Smith 1985: 203–5). This is then applied to the already-fired vessel, and the object is then fired again in reducing conditions to red-heat so that the metals change into their elemental form and fuse to the surface. It is a very demanding technique. If any oxygen gets into the kiln the metals vaporize (hence the ochre in the clay, as oxygen would rather be with the iron); if the kiln is too hot, the entire pigment, including the clay, fixes to the surface; if the firing is too long the metals sink into the surface of the glaze rather than being a metallic lustre on the surface.

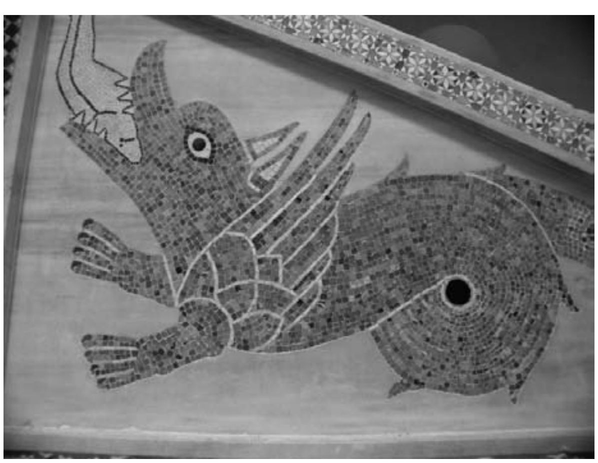


Figure 2: The ambo of the Duomo of San Pantaleone, Ravello. Width of image c. 90cm.

Distinguishing between one type or style of ware and another normally involves a whole host of variables, including the vessel form and the very nature of the ceramic body itself, which may not be useful when considering characteristics useful for distinguishing fragments no bigger than a finger nail of which you cannot see either the other side or any of the sides at all. Hence the following discussion will be restricted to properties that are relevant to the Italian mosaic tesserae, and are not all the distinguishing features of the groups as defined.

The earliest lustre-painted pottery appears to have been made in Iraq, at Basra (Mason 1997a, 2004: 23–60). Another technique first developed in this region, most likely in Basra itself, is the opacification of the glaze by the addition of tin-oxides. This technique seems to have started around AD 700 at Basra, and again can probably be related to glass-making techniques in Syria (Mason and Tite 1997). The Basra body is a fine yellow-buff clay, but this would be obscured by the opaque glaze if we were considering this ware as potential tesserae. The lustre-pigment itself, applied from about AD 800, is often polychrome initially, but in the tenth century it is a uniform greenish lustre, most likely rich in silver.

In about AD 975 the lustre-potters seem to have ceased production at Basra, and commenced production at Fustat, or Old Cairo in Egypt. Lustre wares made in Egypt can be divided into four groups, which I consider to represent successive phases roughly dated AD 975–1025, 1025–1075, 1075–1125 and 1125–1175 (Mason 1997b, 2004: 61–90). The first group is very similar to the immediately preceeding Basra wares, with tin-opacified glazes over a buff clay body, but differs in that the lustre pigment although still monochrome does not have a consistent colour. Recent analyses by Trinidad Pradell presented at the 2004 Archaeometry Symposium in Zaragosa would indicate that this is due to variability in the pigments themselves. The succeeding group is essentially similar, having a tin-opacified glaze and lustre-pigment of variable hues, but differs in that the lustre-paint often has lines incised into it, revealing the glaze underneath. Some examples in this group also have coloured tin-opacified glazes, particularly copper-turquoise. The final two groups differ significantly in their technology. They have a different ceramic body, it being a dense red calcareous clay, and have no tin in the glaze although it is still fluxed with lead and alkalies (see Table 1). Lead is not an essential part of tin-opacified glazes, but it makes the oxidation of the

tin much easier, so it is always present and normally introduced into the glaze mix with the tin. Presumably the objective in adding the lead was that the pottery would perform during both the main and lustre firings in exactly the same manner as the tin-opacified glazes. Hence to create a white vessel that had a red clay body and a transparent glaze a different technique was used, although exactly how it was achieved is difficult to tell. In magnification (see SEM micrograph in Mason and Tite 1997: fig. 10) this can be seen to be a layer of crystallisation on the glaze-body interface, comprising calcium-silicate wollastonite crystals. So when looking through the glaze, for instance while standing in a Ravello church and examining it with a 10x hand-lens, what would be seen is a clear glaze, and then a layer of white acicular crystals.

At about the same time as the Fustat potters switched from a tin-opacified glaze to a clear lead-alkali glaze, c. AD 1075, some of the potters left again to set up production in Syria (Mason 1997c, 2004: 91–120). The first group of Syrian lustre wares are often called 'Tell Minis' wares in the literature, and were probably made in Western Syria. Of all the lustre-wares made in the Middle East, this is the only one for which I have been unable to determine a production centre, and is one of the reasons I have been undertaking fieldwork in Syria for the past several years (Mason and Gonnella 2000; Mason 2003). It is a short-lived centre, its end probably motivated by the activities of Crusaders in the region after AD 1099, notably the sack of Ma'arrat al-Nu'man. All 'Tell Minis' wares have a body of stonepaste. From various technical treatises and studies of this material in later periods we have a recipe for this paste as comprising about 8 to 10 parts quartz, one part of clay, and one part of glass (Mason and Tite 1994). This technology first developed in Egypt, based on prototypical practice in Iraq and Egypt (see also Mason and Keall 1999). The 'Tell Minis' wares represent the first time that lustre-wares were entirely found on stonepaste, as earlier Egyptian wares were found on clay bodies also. Like the contemporary group 3 and 4 lustre-wares in Egypt, the 'Tell Minis' wares are of clear lead-alkali glazes, except for rare exceptions of tin-opacified glazes. Hence the fine stonepaste body is visible through the glaze. Sometimes the glazes are coloured cobalt-blue. It is interesting to note that both Egyptian and Syrian lustre-wares made after c. 1075 lack tin, and perhaps this is because of problems in supply. Lead-isotope studies indicate a switch in lead source at the same time from western to eastern Mediterranean sources (Wolf et al. 2003). Like the group 2 Egyptian lustre wares, the 'Tell Minis' wares also have lines incised through the lustre paint, which is itself a uniform greenish hue resulting from high silver content.

When the 'Tell Minis' manufactory ceased production between 1100 and 1125, the potters moved to a number of centres, notably Damascus and Raqqa in Syria, and Kashan in Iran. All later lustre-wares in Syria have a transparent alkali glaze, which tends to be thicker than the lead-alkali glazes and will have a faint green tinge from the presence of iron. The stonepaste body is distinctly coarser and more granular than that of the 'Tell Minis' wares. They also uniformly have a brown copper-rich lustre-paint. None have incision through the lustre-paint.

Kashan wares form a long sequence of production up into the 14th century (Mason 1997d, 2004: 121–155). These can be quite variable, sometimes having alkali or tin-opacified glazes, the latter more common, usually with a brownish copper-rich lustre-paint. They may have incision through the glaze, but this is more common with styles made after c. 1200, which have a sequence of very distinctive motifs incised

Table 1: Glaze chemistry

Type	No. of samples	SiO_2	PbO	Na_2O	K_2O	CaO	Al_2O_3	SnO_2	MgO	FeO
Pre-Islamic glazes	4	65.0	0.0	12.5	4.7	7.9	3.4	0.0	3.8	2.3
Iraqi alkali glazes	10	60.2	1.0	9.5	3.5	5.5	3.9	0.0	1.8	1.0
Typical Basra tin-opacified	8	62.1	7.9	6.8	4.2	4.8	1.5	9.1	2.7	0.5
Fustat tin-opacified glazes	10	47.4	31.8	3.7	1.6	2.2	1.6	10.0	0.3	0.7
Fustat lead-alkali glazes	8	56.9	22.8	8.2	2.5	4.3	1.3	0.1	1.0	1.0
Syrian lead-alkali glazes	4	63.4	17.1	11.3	1.6	3.5	0.9	0.1	1.1	0.5
Syrian alkali glazes	10	69.1	0.1	17.3	1.9	6.2	0.5	0.0	1.3	0.8
Kashan tin-opacified	14	56.3	19.4	8.8	1.3	3.9	1.4	6.5	1.2	0.8
Iranian alkali	11	71.1	0.0	14.5	2.1	5.9	0.8	0.0	1.8	1.0

For methodology etc., see Mason 2004: 35, 72, 102,135.

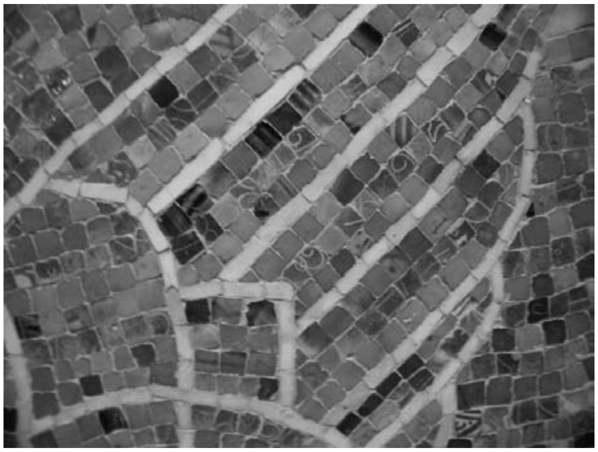


Figure 3: Detail of mosaic on the ambo of the Duomo of San Pantaleone, Ravello. Indiviual tesserae are c. 1.0–1.5 cm diameter.

through the paint, including spirals, then ear-muff shapes, then dots. Inscriptions are also found incised through the paint.

So, back in Ravello, the fragments of lustre-ware in the mosaic (Fig. 3) all have tin-opacified glazes, tend to have different hues of pigment, and have incised lines through the lustre-paint.

Monochrome-glazed wares

The monochrome-glazed wares are of four main types. There is a tin-opacified glaze that is coloured copper-turquoise, a clear copper-turquoise, a clear copper-green, and a clear cobalt-blue. The clear glazes often have lines incised in the underlying body, which is of a coarse stonepaste.

The opaque glazes actually have occasional traces of lustre-ware on them, so it is likely that these are in fact all lustre-wares. Otherwise tin-opacified monochrome glazes tend to be contemporary with lustre-wares of a similar nature, for instance the second group of Fustat lustre-wares, or Iranian lustre-wares of the full sequence of production.

The clear glazes are from what I call incised wares (e.g., Mason 1997b, 2004: 61–90). They have a stonepaste body, decoration obtained by incising into the body, and a clear glaze which is often coloured, and by pooling in the incision will accentuate it. The earliest of these was made in Egypt contemporary with group 2 lustre wares, c. AD 1025–1075, continuing in production until around 1100, and are the first wares entirely made of stonepaste. They may have been made to emulate imports of Sung porcelains from China. I say emulate as the earliest seem to be identical in forms and motifs to the lustre-wares. These have a lead-alkali glaze that presumably could have been fired under the same conditions as the tin-opacified wares (see Table 1). The glazes are generally coloured copper-green, copper-turquoise, manganese-purple, cobalt-blue, or iron-yellow, or are colourless and splashed with cobalt blue. These colours seem to be found throughout the complete sequence.

When the potters moved to Syria this technique was also brought along with the lustre-wares. However, from the material I have studied, notably the entire excavated corpus of Aleppo (Mason and Gonnella 2000; Mason 2003) and also Tell al-Acharneh which has a significant number of these wares, the only colours found are the colourless with cobalt-blue splashing, copper-turquoise, and cobalt-blue. All the other colours, notably including the copper-green found at Ravello, are absent. Similarly all later incised wares in Iran and Syria have an alkali glaze, which would provide a challenge in the production of a copper-green glaze. The conventional wisdom for copper-coloured glazes is that alkali glazes are turquoise (at least when first made) and lead glazes are green. Deterioration may interfere with this, but that is not an issue with the glazes we are considering here. How a lead-alkali glaze with copper in it will be green in one instance and turquoise in another is something that requires further investigation.

San Giovanni del Toro, Ravello

The church of San Giovanni del Toro in Ravello contains a marble pulpit (Fig. 4) similar to the Ravello Duomo pulpit dated to the early 13th century. This also has a mosaic of the whale swallowing Jonah made of pottery from the Middle East, and also has several roundels made of pottery. Such roundels are often termed *bacini* and are well known in other Italian churches, of which the best published are those of Pisa (Berti and Tongiorgi 1981).

The mosaic (Fig. 5) contains pieces of pottery which have clear copper-turquoise glazes over a stonepaste body, which are otherwise featureless. But what these actually are is indicated by a couple of tesserae in a border mosaic to the left of the figure. These have black lines painted in two arcs across the fragment, which can be seen to be on the surface of the body rather than the glaze. These are under-glaze painted wares. This technology first developed in Syria, probably Damascus, and may be related to the switch in glaze technology noted in the difference between 'Tell Minis' and later Syrian lustre-wares. An uncommon ware contemporary with the 'Tell Minis' lustre-painted and incised wares is what is

Figure 4: Pulpit of San Giovanni Del Toro, Ravello.

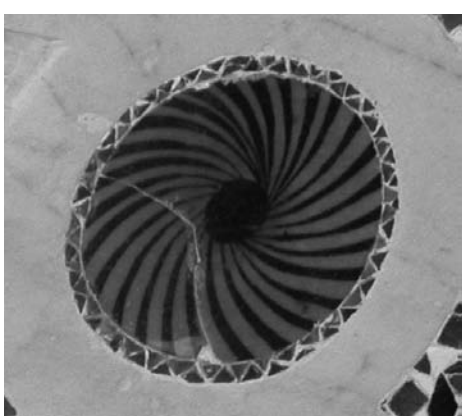
Figure 5: Mosaic on the pulpit of San Giovanni del Toro, Ravello.

often called 'Laqabi' ware in the literature. This has a stonepaste body, which is then incised and carved with a figural representation (closely related to the incised wares), and is then painted with oxide colourants (cobalt-blue, manganese-purple, copper-turquoise being common) and then covered with the lead-alkali glaze typical of the 'Tell Minis' group as a whole. The lead content of the glaze tends to make the pigments run, and so the design is primarily defined by the carved lines. The switch to an alkali glaze would have made the carving unnecessary, as the colours would not run, and under-glaze painting was invented. Apart from copper-turquoise glazed and chromium-black under-glaze painted wares there were polychrome wares with colourless glazes and chromium-black, cobalt-blue and iron-red paints (Mason et al. 2001).

Under-glaze painted wares have a long period of production, indeed similar wares are still being made today in Iran, but the arcuate lines are actually a very particular motif found on Syrian under-glaze painted wares, particularly those made in Damascus. The 'arc-back' group was made in about 1150–1200, mostly in Damascus.

Of the *bacini*, two examples are lustre-wares. They have clear cobalt-blue glazes over a fine stonepaste body, and broad applications of lustre-paint which are incised. Hence these must be of the 'Tell Minis' group from Syria (see above). One example is actually of fish, originally four fish radiating from the centre with their noses touching, and very similar fish can be noted on other 'Tell Minis' wares (Porter and Watson 1987: cat. Nos. A20, A21).

The remainder of the *bacini* are all under-glaze painted wares, both copper-turquoise and chromium-black, and polychrome. Attribution of



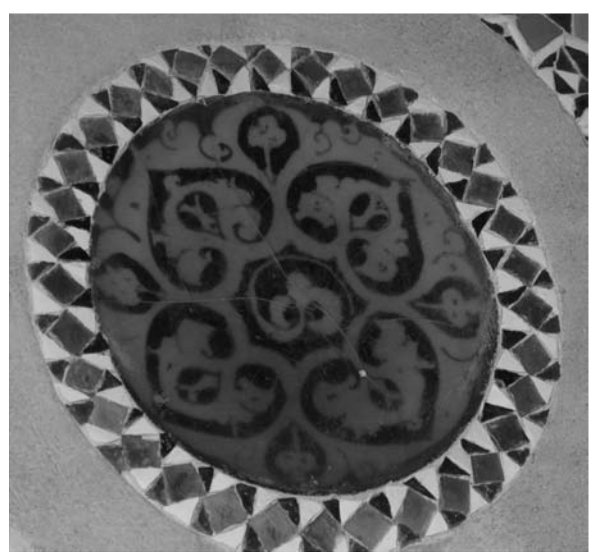


Figure 6 (left) and Figure 7 (right): Detail of pottery in the pulpit of San Giovanni del Toro, Ravello. Diameters c. 15–20 cm.

these wares is entirely stylistic, but they are certainly all Syrian, probably from Damascus, and individual designs can be related to examples of the late 12th century (e.g., Fig. 6, compare to Mason 1997c: fig. 18, ASH.33; and fig. 19, ASH.32), while others can be attributed to the early 13th century (e.g., Figure 7 can be related to designs on lustre-wares of the early 13th century, see Mota 1988: cat. No. 14).

Discussion

From consideration of the attributes of lustre-wares made in the Middle East it would seem evident that the lustre-wares found as tesserae in the Ravello Duomo ambo mosaic are those classified as group 2 of the Fustat lustre-ware sequence, dated to c. AD 1025–1075. Similarly the monochrome opaque copper-turquoise glazed wares are also of this same group. The incised wares could be from up to AD 1100, but it is possible that they are of exactly the same date. The date sequence I have developed for the Egyptian wares is only as precise as the broad time-range would suggest, but I am completely confident that they postdate the first decades of production in Fustat for which there is dateable evidence, and predate by some decades the Crusades, which form an event horizon in the region where they occurred, so they are from somewhere in this chronological vicinity. But the real point is that they form a coherent recognizable contemporary group. It is possible that the pottery used to make the Ravello Duomo ambo mosaic was made in a single firing, and most certainly could have been a single shipment. Interestingly, many of the published lustre-wares from Pisa (Berti and Tongiorgi 1981) are of exactly this origin (Mason 1997b).

The San Giovanni del Toro pottery, however, seems to be selected from a much longer time-span. The two 'Tell Minis' wares would be dated from c. AD 1075 to possibly as late as 1125, the bulk of the underglaze painted wares to the second half of the 12th century, and a few to the first half of the 13th century. This would reflect a time-range of 100 years at the very least.

The differences between the two assemblages may reflect a very different mechanism of procurement. The Ravello Duomo pieces may reflect a single shipment directly from the manufacturers, or as direct as is normal in the world of medieval commerce. As such it would reflect the significant and peaceful trans-Mediterranean trade of the period before the Crusades, particularly with Egypt. The San Giovanni pieces are from the period of the Crusades. The large caches of 'Tell Minis' wares found in caves in western Syria probably reflect valuables hidden from the Crusaders, and the Crusader castle at Tell al-Acharneh contains a significant amount of these wares taken as loot. The later wares may be loot, or reflect the more peaceful co-existence that developed between Crusader states and the Islamic world after the first few decades. Hence it may be that these ceramics were obtained as a group from the Crusader states, or even reflect material brought back by Crusaders or the merchants that traded with them.

Acknowledgements

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Note

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Chapter 5

Some implications of the use of wood ash in Chinese stoneware glazes of the 9th–12th centuries

N. Wood[1]

'The misty scenery of late autumn appears when the Yue kilns are thrown open: The thousand peaks have been despoiled of their bright colours for the decoration of the bowls.' (Bushell translation)

'In the chilly autumn in September, thousands of porcelain wares as green as peaks appear from the kilns.' (Modern Chinese translation)

Lu Guimeng. 9th century poet.

Abstract

South China's ancient and long-running ash-glazed stoneware tradition (c 1500 BC to AD 1200) seems to have used c. 30–50 wt% of dry calcareous wood-ash in its original glaze recipes. When it is calculated how much ash would have been needed for these glazes it appears that this was far more than could have been provided by ash recovered from kiln-firings. It seems likely that much of this glaze-ash was prepared especially – adding greatly to the fuel-demands of this huge and ancient tradition. Thus some hitherto unexplained movements and extinctions of south Chinese ash-glazed kiln-complexes may have owed something to the effects of deforestation.

Introduction

Sometime towards the middle of the second millennium BC, potters in the south of China developed the world's first glazed stoneware, much of it fired to temperatures in excess of 1200°C (Yuba 2001; Zhang Fukang 1986: 40). For the next two and a half thousand years stoneware remained China's main glazed ceramic production, before porcelain gradually replaced the material at many kiln sites between the 7th and the 13th centuries AD. Nonetheless, until the early 6th century AD most stoneware-making was confined to southern China, while the north made largely earthenware, most of it unglazed. To some extent this may have been a geological effect, as the old North China Block had very different raw materials from those found in the south (Wood 2000). North China was certainly not a backward area, as it had seen the emergence of many material and cultural features that we now associate with China's great agricultural civilisation, but its high-temperature ceramics were rather slow to become established.

In greater detail, the success and continuity of south China's long-running stoneware tradition seem to have depended on three essential elements:

- The use of naturally siliceous stoneware clays, abundant as surface deposits throughout southern China.
- The use of the dragon kiln principle, where long sloping tunnels were built up hillsides and the wares fired inside by wood and/or by scrub.
- A simple and effective method for glaze-making that combined body-clays with calcareous wood ashes to create stoneware glazes.

This last technique produced glazes that matured in the 1170–1240°C range. Reduction-firing was common for both earthenwares and stonewares throughout southern China from the Bronze Age onwards, and this meant that many southern stoneware glazes were grey-green in colour from their iron and titanium oxide contents, supplied by their clay and ash constituents. These grey-green glazed stonewares are often known today as 'Yue wares' or 'Yue-type wares' after their main production centres in the region of China once known as the State of Yue, with its heartlands in northern Zhejiang and southern Jiangsu provinces (Cai Naiwu 1994: 26–40; Li Jiazhi 1986).

Oxidised ash-glazed stonewares were also made at kiln-complexes such as Tongguan in Hunan province and Qionglai in Sichuan province in the later Tang Dynasty (Tang, AD 618–907). These latter wares showed the warmer colours characteristic of glazes coloured by Fe^{3+} ions. The ambers and browns were often supplemented with greens and purple-browns, achieved by using small amounts of copper- and manganese-rich minerals, respectively, as glaze-colouring agents. Liquid-liquid phase-separation effects were also exploited at Tongguan and Qionglai during this period to give cream and off white semi-opaque glazes. Nonetheless, all these varied compositions were essentially mixtures of siliceous stoneware clays with substantial amounts of wood ash, with the latter comprising some 30–40 per cent of the glaze (Zhang Fukang 1987, 1989).

By the late 9th c. AD, a few decades before true white porcelains were first made in south China, the southern ash-glazed stoneware tradition was at its height, with many kiln sites also contributing to major export trades. Ash-glazed stonewares were made in most southern provinces, including Zhejiang, Fujian, Jiangxi, Jiangsu, Anhui, Hubei, Hunan, Sichuan, and Guangdong. Wares from all these regions used the same three principles – that is siliceous stoneware clays, 'dragon' kilns fired with wood, and the clay-and-ash technique to make their glazes, with the presence of wood ash indicated by the relatively high levels of phosphorous and manganese oxides in the glazes' compositions (Zhang Fukang 1989). A heavy consumption of wood and scrub, both for firing the kilns and for making glazes, was therefore an essential feature of this vast, productive and widespread industry, and it is the relative consumption of wood-ash in glazes and in kiln-firing that is the subject of the present paper.

Use of wood ash in stoneware glazes

China has always made extensive use of calcareous ashes in its stoneware glazes. This is due partly to the temperate climates of the stoneware-producing areas of China that encouraged the types of vegetation that yielded ashes of this high-CaO type. But calcareous ashes were also used from choice, as the high temperatures employed favoured calcium oxide as a prime glaze-flux. It is not hard to see how increasing firing temperatures in Shang dynasty (16th–mid 11th centuries BC) kilns led gradually to natural glazing of the wares from fly-ash – an effect that was soon imitated by the Shang potters' deliberately applying wood-ash to their wares before they were set in the kilns for firing (Zhang Fukang 1986). From this approach grew true slip-glazes made from mixtures of body-clays with wood-ashes. Once established, glazes made from such clay-and-ash mixtures came to dominate stoneware production throughout southern China. Siliceous stoneware bodies, bearing these glazes saw their most prestigious and productive expression at the late Tang kilns of north-eastern Zhejiang province, where the best quality Yue wares were made.

Glaze compositions

South Chinese ash glazes, from the Shang to the Southern Song periods show an unusually consistent chemical make-up that corresponds broadly to the 1185°C calcia-alumina-magnesia-silica eutectic mixture, sometimes abbreviated to CAMS (SiO_2 63.0, Al_2O_3 14.0, CaO 20.9, MgO 2.1, as wt%, see Table 1). This mixture has a silica-alumina ratio of 4.5:1 in real weights, similar to those found in typical south Chinese stoneware clays (see Table 2). These siliceous stoneware clays were often refined from primary rocks and are found within a geological domain that shadows the old South China block (Wood 2000: 15–22).

Additions of calcia- and magnesia-rich materials to these clays (readily supplied by calcareous wood-ashes with lesser magnesia contents) made stoneware glazes easy to manufacture from local resources. Analysis and replication suggest that the best recipes for meeting the 'eutectic demands' of the CAMS

Table 1: Analyses of southern stoneware glazes: 1st to 11th C AD.

Dynasty or period	**Kiln**	**Province**	**SiO_2**	**Al_2O_3**	**TiO_2**	**Fe_2O_3**	**CaO**	**MgO**	**K_2O**	**Na_2O**	**P_2O_5**	**MnO**	**Totals**
Eastern Han	Shangyu[1]	Zhejiang	57.9	13.7	0.6	1.6	19.7	2.4	2.0	0.7	0.9	0.9	100.4
Eastern Han	Shangyu	Zhejiang	58.95	12.75	0.7	2.0	19.6	1.9	2.2	0.8	0.8	0.2	99.9
3 Kingdoms	Shangyu	Zhejiang	60.9	13.8	0.5	2.0	16.9	2.2	1.9	0.8	0.8	0.3	100.1
Tang	Wenzhou	Zhejiang	63.7	11.7	0.6	1.9	15.1	2.7	1.6	0.8	1.6	0.4	100.1
Tang	Yuyao	Zhejiang	61.3	13.1	0.5	1.5	16.6	1.6	2.6	0.4	1.0	0.6	99.2
Tang	Yixing	Jiangsu	62.8	11.7	0.7	2.0	15.5	2.8	1.6	0.8	1.7	0.4	100.0
Tang	Yixing	Jiangsu	59.8	12.6	0.35	2.1	17.5	2.6	1.6	0.9	1.7	0.45	99.6
Tang	Qionglai	Sichuan	56.9	12.1	0.7	1.8	20.3	2.0	2.3	0.2	2.3	0.3	98.9
Northern Song	Yongfu	Guangxi	56.8	13.9	0.8	1.5	20.6	3.8	1.3	0.3	1.2	0.1	99.5
Five Dynasties	Jingdezhen	Jiangxi	62.2	14.8	0.3	1.4	17.2	1.3	1.9	0.3	0.7	0.2	100.3
Average			**60.1**	**13.0**	**0.6**	**1.8**	**18.0**	**2.2**	**1.7**	**0.8**	**1.3**	**0.4**	100.0
65 siliceous clay													
35 washed wood ash (Experiment at the British Museum by NW in 1993)[2]													
			60.6	12.7	0.8	2.7	19.0	0.8	2.1	0.8	1.8	0.4	101.7
1,185°C SiO_2-Al_2O_3-CaO-MgO eutectic mixture[3]			**63.0**	**14.0**			**20.9**	**2.1**					**100**

[1] Guo Yanyi et al. (1980), p. 237, table 3.
[2] Wood (1994), p. 47, table 1
[3] Tauber and Watts (1952), p. 458

Table 2: Siliceous stoneware bodies of southern China, 13th C BC to 11th C AD.

Dynasty and kiln site	**Province**	**SiO_2**	**Al_2O_3**	**TiO_2**	**Fe_2O_3**	**CaO**	**MgO**	**K_2O**	**Na_2O**	**Totals**
Mid Shang[1] Wucheng	Jiangxi	73.9	18.1	1.2	2.6	0.2	0.65	1.7	0.3	98.65
W. Zhou[2] Shinmendamashan	Zhejiang	76.1	17.4	1.0	1.9	0.25	0.3	2.9	0.5	100.35
E. Zhou[3] Yixing	Jiangsu	75.7	16.2	1.0	2.2	0.3	0.5	2.1	0.7	98.7
Tang[4] Changsha	Hunan	72.9	19.7	0.8	1.6	0.1	0.6	3.05	0.15	98.9
Tang[5] Qionglai	Sichuan	75.4	16.1	1.0	3.2	0.25	0.9	2.1	0.4	99.35
N. Song[6] Huizhou	Guangdong	72.4	21.8	1.1	1.9	0.5	0.8	2.1	0.3	100.9
N. Song[7] Yongfu	Guangxi	73.9	19.2	1.1	1.9	0.5	0.8	2.1	0.3	99.8
Average		**74.3**	**18.35**	**1.0**	**2.2**	**0.3**	**0.65**	**2.3**	**0.4**	**99.5**
(Av. SiO_2 : Al_2O_3 ratios 4.1:1)										

[1] Li Jiazhi et al. (1992), p. 4, table 1
[2] Li Jiazhi et al. (1986), p. 57, table 1
[3] Luo Hongjie (1996), database.
[4] Zhang Fukang (1987), p. 90, table 1
[5] Zhang Fukang (1989), p. 63, table 1
[6] *Ibid.*
[7] Luo Hongjie (1996), database.

composition were achieved by using 30–50% of wood ash mixed with body clay, or its close equivalent, by dry weight (Wood 1999: 32). In practice, potters often combined ash or clay suspensions in the forms of slips to make their glazes (Meng-Chang Ling 1947: 7). This would have provided working recipes different from the above, but the final suspension-blends would still have contained some 30–50% wood ash.

Preparation of ash

Besides the oxides of silicon, aluminium, calcium and magnesium, most Chinese wood ashes also contain oxides of potassium and, to a lesser extent, sodium. These last two elements tend to occur in wood-ashes in the form of soluble carbonates. These alkalis are often deliberately eliminated from wood ashes used

Table 3: Wood ash from Fujian province, before and after washing.[1]

	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	MnO	Loss	Totals
Ash (unwashed)	11.95	6.1	trace	0.9	33.6	5.8	10.9	0.2	1.85	2.85	24.4	98.55
Same ash washed	11.0	2.9	trace	0.8	40.5	5.7	2.1	0.1	1.9	2.8	32.2	100

[1] Chen Xianqiu et al. (1986) p. 237, table 3

for glazing, as they tend to make the glaze-slips caustic. Soluble alkalis may also cause problems by diffusing into the clay bodies, and also crystallising on the surfaces of the glazes before firing. They also make it difficult to adjust the consistency of glaze-slips successfully by pouring away surplus water as, with large amounts of soluble alkali in a glaze, any loss of water means a loss of flux and a change in the glaze's melting point. For all these reasons 'washing' of ash was (and is) practised in many pottery-making traditions, in order to remove an excess of soluble alkali. This is a rather different approach from glass-making, where the alkali content of ash is highly valued and the materials are used dry.

An example of how washing may change an ash's chemical constitution may be seen in Table 3, where a wood ash used by modern potters in Fujian province is reported both before and after the process. It can be seen that most of the compositional difference occurs in the level of potassium oxide, which drops sharply with the treatment.

In Japan and in modern western craft-practice wood-ash is often prepared by steeping the material in water, allowing it to settle, and then carefully tipping away, or siphoning away, the discoloured water above the ash. This liquor is quite caustic, and the first steeping removes a high proportion of the soluble alkali. After this liquor has been discarded fresh water is added, the ash and water are stirred, and then allowed to settle once more, after which the supernatant water is again removed.[2] Robert Tichane has shown by experiment that about ten per cent of the ash's weight may be extracted by this process, mostly in the form of soluble potassium salts (Tichane 1987: 62). In China another method was often followed, namely placing the wood-ash in a densely woven bag, submerging the bag-plus-ash in water, and allowing the alkalis in the ash to diffuse away (E-Tu Zen Sun and Shiou-Chuan Sun 1966: 144–5).

Wood ash residues from burning different plants

The ash-yield from the burning of timber, stalks, scrub or leaves tends to be small, typically from 0.2 to 6.5 per cent of the original weight of the dry material (Table 4).

With siliceous botanic materials (such as bracken, rice straw, sorgum stalks, etc.) the amounts of ash produced by burning tend to be nearer to four per cent. With low-silica woody materials (particularly the hardwoods and softwoods) the figures are nearer to the lower end of the range (0.4%), and the ashes that result are far richer in calcium and magnesium oxides (Table 4) (Tichane 1987: 30) and often with silica/alumina ratios near to the CAMS mixture. Thus many of the ashes used for glazing stonewares in southern China may have derived from botanic materials that yielded only 0.4% of ash. This yield would have been further reduced by the washing process, taking the 0.4% nearer to about 0.36%. Washing of ash may be suspected in many Yue and Yue-type glazes because of the unusually low levels of alkalis reported in their compositions (Table 1) (Wood 1999: 32–3).

Sources of wood ash

One might imagine that the firing of dragon kilns to stoneware temperatures would provide constant and abundant supplies of wood ash, suitable for stoneware glazes. Unfortunately, in practice, most of the wood-ash from the firebox, or from the side-stoking, of a dragon kiln is carried into the kiln where it fuses to walls and saggars, or is carried out of the kiln by the draught of the fire.[3] There is also the issue that dragon kilns are quite efficient in operation. This means that the weight of wood needed to fire a dragon kiln may be only the equivalent of the weight of the setting being fired.[4] As only 1/250th (0.4%) of the weight of the original fuel would survive as ash, this would fall far short of the ash needed to glaze all the pots in a setting – even assuming that all the wood-ash generated by firing could be recovered, which is far from being the case.

Glazed stoneware traditions in south China that used wood ash must therefore have relied on sources other than kiln-ash for the majority of their glaze-ash supplies. In small Japanese country potteries two additional sources have been described: from house-

Table 4: Ash yields of various trees and plants (unwashed).[1]

Analyst	Material	Per cent ash	
Misra *et al*	Spruce wood	0.21	
Misra *et al*	White fir wood	0.24	↑
Wolff	Pine wood	0.33	
Misra *et al*	Aspen	0.43	increasing
Misra *et al*	Yellow poplar	0.45	calcia
Wolff	Beech wood	0.46	
Wolff	Oak wood	0.49	
Misra *et al*	White oak	0.87	
Wolff	Pine needles	1.4	increasing
Misra *et al*	White oak bark	1.64	silica
Misra *et al*	Douglas-fir bark	1.82	
Wolff	Cotton stalks	2.8	
Wolff	Sorgum stalks	3.7	↓
Wolff	Ferns	6.5	

[1] Compiled from Tichane (1987), p. 31, table 6.1 (quoting Wolff (1880)), and Misra et al. (1993), p. 104, table 1

hold hearths (Sanders 1967: 99) and from textile workers who had already extracted from wood ash the soluble alkali for use in dyeing (Cort 1979). However, it seems unlikely that similar sources could have satisfied the huge demand for wood-ash for the Chinese stoneware industries of the 9th c. One can suspect that much wood ash at this time was obtained by burning wood, scrub, leaves or stalks – in many cases solely and deliberately for use in glazes. It is also doubtful whether the burning of agricultural by-products such as crop-stalks and hulls could have provided much ash for the potters, as these materials were valued by farmers as cooking and heating fuels, and animal bedding, so were hardly surplus to requirements. Even so the ashes of any materials burned by farmers could perhaps have been reclaimed from local hearths or stoves, in the Japanese manner. Nonetheless, the scale of Japanese and Chinese ceramic enterprises tended to be very different. Large domestic and huge export markets were served by the Chinese kiln-complexes of the 9th c. AD, and higher percentages of wood ash tended to be used in the Chinese glazes, with 30–50 wt% ash being typical amounts in most southern kilns during this period.[5] The quantities of ash consumed for glazes in south China in the 9th c. must therefore have been formidable.

How much wood-ash is present on a glazed stoneware bowl?

It is possible to make some assessment of the proportion of wood ash that is present in the glaze of a fired Yue ware bowl, compared with the bowl's total weight. This can be managed by reference to published figures. Numerous data exist of the thicknesses of glazes on Yue wares, compared with the thicknesses of their bodies – with typical measurements being 0.25 mm for the total glaze thickness (inside and out) and 4.5 mm for the body. Glaze cover on late Tang dynasty Yue ware bowls is practically total.

As the specific gravity of a fired stoneware glaze is comparable to that of fired stoneware clay (typically about 2.6 g/cm^3 for the glaze and the body) the relative weights of the glaze and the clay that comprise a bowl can be calculated from these figures (Table 6).[6]

We also know that some 40% by weight of the glaze will be wood ash, with the remainder clay, so the weight of the glaze should be multiplied by 0.4 to give the weight of the ash. In many cases the results of these calculations show that wood ash represents some 2–5% of the weight of a fired Yue ware bowl. So, for example, a small glazed Yue ware bowl that weighed 200 g might have had an ash-content in its glaze of 4–10 g. At 0.36% ash-yield from burning+ washing, the weight of wood needed to supply this ash would have been 277.7 g [i.e. the weight of wood needed to supply 1g of ash at 0.36% ash-yield] x 4–10 – that is some 1111 g to 2777 g of wood (see Table 6 for more worked examples).

How would this compare with the weight of the wood that was needed to fire the bowl? With once-firing (i.e. no preliminary biscuit-firing), an open setting (i.e. no saggars, but 'stem' supports), and a typical dragon kiln efficiency of the weight of the fuel equalling the weight of the ware being fired, this would mean 400 g of wood would have been needed to fire the bowl and its support. This assumes an equal weight of 'kiln furniture' and ware. Thus, for open-firing, between two and seven times as much wood might have been consumed in making glazes for Yue ware bowls as was used to fire them. With the use of saggars (typically five times the weight of the wares they contain) the balance shifts considerably, with slightly more fuel now often used to fire the bowls than to glaze them. In practice a mixture of saggar- and open-firing would have operated in most Yue ware kilns of the later Tang dynasty.

These are perhaps surprising and significant figures as they suggest that the fuel consumption involved in the preparation of ash for the making of glazes may have been at least as high as the fuel-consumption of the kilns – and in many cases a great deal higher. Given the huge scale of the Yue ware and related industries in pre-Song China, this implies that the preparation of wood ash for making glazes could have had at least as much impact on the environment as the collection of wood for kiln firing.

Another particularly wood-hungry ceramic

Table 5: Analyses of typical Far Eastern calcareous ashes (n.t. = not tested)

High calcia ashes	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	MnO	Loss	Totals
Wood ash, Shenhou Henan [1]	20.8	4.1	0.3	1.35	34.1	3.0	3.9	0.3	1.9	0.3	30	100.05
Fujian wood ash (washed) [2]	11	2.9	trace	0.8	40.5	5.75	2.1	0.1	1.9	2.8	32.2	100.05
Hearth ash, Japan [3]	14.1	3.7	n.t.	0.9	35.9	5.4	1.5	0.5	2.1	0.1	34.3	98.7
Wood ash, Henan province [4]	16.7	2.6	n.t.	1.7	39.6	2.8	2.8	0.3	1.5	n.t.	31.7	99.7
Average:	**15.65**	**3.3**		**1.52**	**37.5**	**4.2**	**2.6**	**0.3**	**1.85**	**0.8**	**32.05**	**99.5**

[1] Guo Yanyi (1987), p.16.
[2] Chen Xianqiu et al. (1986), p 237
[3] Cardew (1969), p. 54, table 5.1
[4] He Haozhuang et al. (1985), p. 18. (Data from poster-paper)

tradition in south China was the manufacture of Guan ware at Hangzhou in northern Zhejiang province in the Southern Song and early Yuan dynasties. The finest Guan wares were first biscuit-fired unglazed, and then biscuit-fired three or four further times, with new layers of glaze applied between firings (Sundius and Steger 1963: 436–9 and Figure 46). The final firing was to stoneware temperatures. The ash content of a Guan ware glaze can be assessed at being about 30%, but the glaze-to-body ratio could be as high as 1:1. Thus a small Guan ware bowl, weighing 200 g, might consist of 30 g of ash (30% of 100 g of glaze), and have needed some 8.3k g of wood simply to make its glaze. To this must be added the fuel costs of as many as five separate firings – the first four being simply part of the glazing process. This would have made Guan wares exceptionally heavy in their energy-costs – perhaps ten times greater than the Yue wares fired slightly earlier in northern Zhejiang province, and often in the same style of kiln (Menzies 1996: 563).

It seems likely that many regions of China suffered diminishing tree-cover from the demands of the glazed-stoneware industries during the 9th and 10th centuries AD. As Cai Naiwu of the Zhejiang Provincial Museum wrote about Yue wares in 1994:

> "After the middle of the Northern Song Dynasty [11th century], the ceramic industry on the northern Zhejiang plains, the central Zhejiang basin and the coastal areas of south-eastern Zhejiang saw a rapid decline. This was party due to the gradual exhaustion of good clay after long years of celadon production, and partly a result of an acute shortage of firewood for firing the "dragon kilns". (Cai Naiwu 1994: 42).

We may now suspect that the burning of botanic fuel, solely to provide ash for glazes, may also have been a significant contributor to the deforestation described by Cai.

The change to limestone

Sometime in the 10th century AD porcelain makers at Jingdezhen were among the first in the south to move from wood ash to limestone as the main glaze flux – a change indicated by a sharp drop in the P_2O_5 contents of the glazes at this period (Wood 1999: 49 and Tables 12 and 13). A text sometimes dated to between 1214 and 1234 describes burning of limestone to prepare the glaze-flux material, and later texts confirm the practice (Vogt 1900: 566). However the true antiquity of burning (as opposed to simple crushing) in the preparation of limestone for glazes in China) is presently unknown. Burning limestone for glazes in China traditionally involved a two-stage process. First a high temperature burning to produce CaO (quicklime), which weathered to $Ca(OH)_2$ (slaked lime), and then a second, lower-temperature, burning to give $CaCO_3$ (calcium carbonate). This second burning returned the limestone to its original composition, but in a form ideal for glaze-making (Liu Zheng and Xu Chuixu 1988: 532–5). Vogt (1900) describes the use of wood charcoal for the first burning (Vogt 1900: 566). The fuel used for burning limestone at Jingdezhen in the 13th century seems to have been 'mountain brushwood' (Bushell 1896: 220). Burning with fern appears to have been more usual in the 18th century through to the 20th century.[7] Addis describes the process as being repeated seven times (Addis 1983: 63). But even at a proportion of

Table 6: Some typical glaze and body thicknesses established for Yue wares, used to estimate the proportional weight of the fused wood ash in the fired ware and the amount of wood needed to supply sufficient ash to glaze a 200g bowl.

Ware Type	Average glaze thickness	Average glaze thickness x2	Average body	Glaze as % of ware's weight thickness	Glaze's ash content as % of ware's weight (40% ash)	Amount of wood estimated for glazing a 200g bowl (assumes 0.36 % ash-yield)
Jin Yue [1]	0.12 mm	0.24 mm	5 mm	4.58 %	1.83 %	1016 g
Tang Yue [2]	0.13 mm	0.26 mm	4.75 mm	5.19 %	2.1 %	1166 g
N. Song Yue [3]	0.1 mm	0.2 mm	4 mm	4.76 %	1.9 %	1055 g
Tang Yue [4]	0.15 mm	0.3 mm	6.5 mm	4.4 %	1.76 %	977.5 g
Tang Yue [5]	0.2	0.4	6 mm	6.25 %	2.5 %	1388.5 g
Tang Yue [6]	0.25	0.5 mm	5 mm	9.09 %	3.64 %	2021.6 g
Five Dynasties Yue [7]	0.15	0.3	2 mm	13.04 %	5.22 %	2899.2 g

1 Vandiver and Kingery (1985), p. 218
2 ibid., p. 219
3 ibid., p. 219
4 Guo Yanyi et al. (1980), p. 243, table 1
5 ibid.
6 ibid.
7 ibid.

ten tonnes of fuel to one tonne of limestone, this gives a carbonate yield of about 1002 kilos from an eleven-tonne fern-limestone mixture, against about 24 kilos of mixed carbonate (Ca, Mg, K and Na) from burning eleven tonnes of dry fern alone. Limestone-burning therefore represents a far more economical use of botanic fuel for the creation of a glaze-flux.[8]

Lower levels of phosphorus oxides in analysed glazes (a good indicator of whether wood-ash or limestone was the main source of calcia) suggest that this 'limestone technology' spread to southern Zhejiang province in the 12th–13th c. AD, where it was adopted by the huge celadon-ware industry that operated around the market town of Longquan for many hundreds of years (Vandiver and Kingery 1985: 191 and Table III). In Korea and Japan, by contrast, wood ash remained the main glaze-flux in stoneware and porcelain workshops until comparatively recent times (late 19th c.). Korean potters tended to mix wood ash with porcelain stones rather than with body-clays, but seem also to have used about 30–40% of washed calcareous ash in their glazes, in order to exploit the CAMS eutectic mixture (Wood 1994: 46–7). This has been the main glaze-type used in Korea throughout its history of glazed stoneware and porcelain making, and the issues raised in the above discussion apply as much to the Korean celadon tradition as they do to Yue wares. This heavy use of wood ash in Korean glazes for hundreds of years may have been a contributing factor to the way that Korean potters were often obliged to move their kilns, as supplies of fuel ran short.

Some qualifications

The figures used in this discussion are reasonable if, of necessity, somewhat approximate. For example the ash-yields quoted for various woods and plants were measured under laboratory conditions, and would have been lower in practice, as some ash was borne away by the wind during burning. Conversely, some small amounts of ash must have been reclaimed from the kilns after firing, and then used for glaze-making. With the multiple firings used for Hangzhou Guan wares this source may have been significant, although these biscuit-firings should perhaps be regarded as part of the glazing rather than the finishing process. Although bowls were the main products of most Chinese kilns in the later Tang dynasty, hollow wares such as jars and ewers were also made and these were often glazed on the outside only. Another uncertainty concerns the fuel to setting-weight ratios that operated in early Chinese dragon kilns. Nonetheless the calculations do indicate strongly that the consumption of fuel to make ash for stoneware glazes in south China must have been a major element in the overall fuel costs associated in producing the wares.

Conclusion

In south China during the Bronze Age a high-fired ceramic tradition evolved that used substantial amounts of wood ash in its stoneware glazes – often thirty per cent or more of the original glaze recipes. By the 9th c. AD thousands of kilns were operating in

south China using this technology, of which the Yue kilns in north eastern Zhejiang were among the most productive. When the amounts of fuel needed to create wood ash for glazes of this type are considered it appears as if, in many cases, the amounts of botanic fuel needed for glaze-making must have exceeded those used for firing. These amounts would also have been far greater than could have been met from recovered kiln-ash. While bearing in mind the qualifications made above, the calculations cited do indicate strongly that the consumption of fuel to make stoneware glazes in south China must have been a major element in the overall fuel costs associated in producing the wares. This fact may have had some relevance to the adoption of limestone as an important glaze flux at south Chinese kilns in the 10–13th c., and perhaps too had some bearing on the decline of the ash-glazed Yue ware tradition in Zhejiang province over the same period. For imperial wares such as Guan ware high fuel costs for both glazing and firing must have been tolerated because of the exceptional status, and the fine material-quality, of the ceramics produced. But even in this industry a certain amount of production was sub-contracted to the wooded regions two hundred or so miles to the south of the Hangzhou kilns, in an area near the market town of Longquan – a kiln complex that soon changed to limestone as its main glaze-flux, in the southern porcelain manner (Proctor 1977: 16).

Notes

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2 A good description of the technique, based on early 20th C Japanese practice, occurs in Leach (1940), p. 160. Bernard Leach was one of the first western writers to discuss the importance of wood ash in East Asian glaze technology.

3 Père d'Entrecolles, writing of the Jingdezhen porcelain kilns in Du Halde (1737), p. 347, records: — 'I have been suprized to hear that after they have burnt a hundred and eighty Load of Wood in a Day at the Entrance of the Oven, yet on the Morrow there is no Ashes to be found on the Hearth.'

4 Data on Chinese, Korean or Japanese dragon kilns, that supply complete information on firing temperature, size of kiln, weight of ware being fired, and weight of fuel used to fire the ware, are hard to find, as there are usually some key aspect(s) of the formula missing. However a dragon kiln making stoneware plant pots, mostly open-fired, in Singapore in 1995, gave the following figures: — Length of kiln, 42 m; finishing temperature, 1200–1250°C; length of firing 36 hours; total cooling, 72 hours; number of pots in kiln, 3500; weight of wood used in a firing, 6 tonnes. The average weight of a pot seemed to be about 2 kg and the setting was achieved without using saggars. (Personal communication at the Sam Mui Kuang Pottery, Singapore, 1995, operated by the Chuang family.) Another source is Terpstra and Zhu (2001), p. 29, describing a typical Jingdezhen cross-draught *zhenyao* kiln. This took 25–35 tonnes of wood to fire 10–15 tonnes of porcelain work to 1300+°C, excluding the weight of the saggars. Leach (1956), p. 13, gives an eye-witness account of the Onda stoneware kiln in Japan (a multi-chambered wood-burning dragon kiln) and writes: 'The local calculation is that one of the large storage jars, approximating 2' x 2' is raised to the requisite heat by the average expenditure of one bundle of fuel weighing 40 to 50 lbs.' This is a wood-to-ware ratio of 1:1 or less.

5 Derived from calculation and practical replication by the author. See also Girel (1988), p. 17.

6 Sundius and Steger (1963), p. 467, note that the True Specific Gravity (i.e. Specific Gravity that disregards porosity) of stonewares ranges from 2.5 to 2.6. Little is published on the S.G. of glazes, but general estimates can be calculated from the glazes' oxide compositions and the specific volumes of these oxides (the 'Additive Theory', see Scholes (1946), p. 224–226). For the CAMS composition this gives a result of about 2.6.

7 Addis (1983), p. 63; Guo Yanyi (1987), p. 13. Addis identifies the plant used at Jingdezhen in the early 1980s as the fern *Gleichenia linearis*, Guo describes both 'wolf-chicken grass' and 'phoenix tail grass', *Pteris multifada poi,* as being used at both Jingdezhen and Longquan.

8 This assumes an ash yield from fern as 6.5% of the dry weight of the plant (see Wolff in Table 4), and a carbonate content of fern ash as about 40 per cent (see Zhang Fukang (1986), p. 43, table 4.

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Chapter 6

The Hispano-Moresque tin glazed ceramics produced in Teruel, Spain: a technology between two historical periods, 13th to 16th c. AD

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Abstract

In order to provide an extended data base of chemical and textural characteristics of tin-glazed ceramics produced in the Iberian Peninsula since the medieval times, one of the most important workshop areas in the Aragon Kingdom (eastern Spain) has been extensively sampled and its ceramic fragments characterised, this is the case of Teruel. Glazed pottery was produced since the 13th century AD in Teruel, but this ceramic production is especially famous for its tin-glazed pottery, decorated with green and brown designs from the Middle Ages until today, and with blue decoration since the 15th century. The chemical composition and textural characteristics of these tin-glazes prove that some features, as, for instance, cassiterite size and crystal distribution, homogeneity or heterogeneity and temper-inclusion presence or absence, are shared with other contemporary regions that followed a similar evolution. Nevertheless these glazed ceramics have also other characteristics that help us to distinguish them from other productions, and also they show some interesting technological properties.

Introduction

Teruel was founded by king Alfonso II of Aragon in AD 1171. The town soon became the main urban place in the south of the kingdom (Fig. 1). Starting point of most expeditions for conquering the town of Valencia during the first half of the 13th century, Teruel was also used to arrange the migratory flow from the Ebro Valley to settle at new places. This people flowing in ensured the stability of the conquered territories.

Between 1232 and 1245, the conquest of Valencia indicates a change between two really different dynamics. From that moment, the remoteness of the Muslim border and the Mediterranean-market opening from Tortosa and Valencia promoted a real economical movement that, in Teruel, was centred on raw materials especially (wool and leather, and also wood and minerals), as well as some manufactured products. Some proofs of this new development during the second half of the 13th c. are the wooden ceiling of the cathedral, the Hispano-Moresque towers or the Teruel law-code manuscript. And also, but less known, other proof is the decorated ceramic.

In fact, first proofs of tin-glazed ceramic production seem to be dated from the last quarter of the 13th c. This pottery was decorated with green, brown or green-brown designs (Ortega 2002). Previously, since the period of Teruel's foundation, the town had its

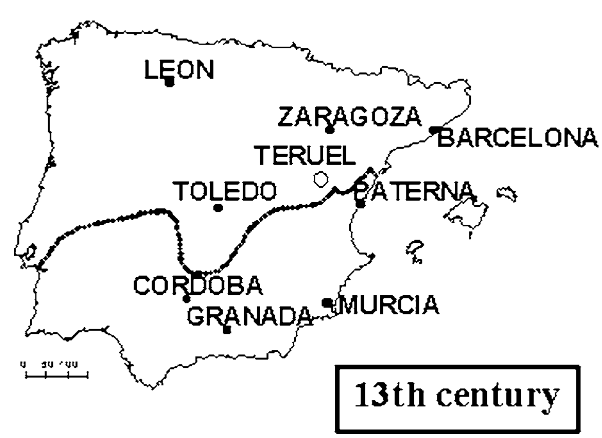

Figure 1: Map of the Iberian Peninsula during the 13th c. AD indicating the border between Christian and Islamic kingdoms. Scale in kilometres.

Figure 2: «Green and brown» decorated pottery from Teruel (14th c.).

own ceramic production of cooking pots and monochrome glazed pottery, in green and honey-yellow colours following Almohad traditions, together with some imports of fine ware from al-Andalus. However, since the end of the 13th c., there was a local production of tin-glazed bowls, hemispherical or with polylobed rims, abundantly decorated, either with simple lines or tangent semicircles in green, or with representational decorations of very thin lines in brown (Ortega 2002). During this period, tin-glazed ceramic was produced at the same time as *ataifores* (big plates), *redomas* (flasks) and small jars glazed in green and honey-yellow colours still very influenced by other contemporary productions from al-Andalus.

In the middle of the 15th c. tin-glazed ceramic distribution covered all southern Aragon and large areas of the border of Castilla, even arriving at Valencia. Then, the commercial capability of Teruel's pottery manufacture gave rise to a progressive standardization of types and decorations. At that moment, there appeared the "classical" patterns, splendidly decorated with "green and brown" designs. A proof of this prosperity is the fact that even jars and plates, before only transparent-glazed, were then tin-glazed and very well decorated with a great variety of designs that combined elements from profane Christian painting, linked to the chivalry culture (for example knights, ladies and mythical animals), with other compositions and designs of a clear Islamic origin (pseudo-epigraphic, geometric, etc.) (Fig. 2).

At the end of the 15th c. the fine designs that characterised the decoration of the last decades became more and more simple and schematic, together with an uncommon evolution of all previous complex patterns, now reduced to a central motif surrounded by some attached micro-elements. The decoration was characterised by the final disappearance of all frames for the motif that was always developed from a central pattern, completed or not with filling elements, especially the very usual series of the brackens. Other formal changes were linked to this transformation of decorative pattern, like disappearance of spherical objects with annular stem and appearance of other similar objects but with a flat base. In the 15th c. there was a tendency to produce open forms with a flat or slightly concave base, together with ear-handled bowls and flat plates with wavy rim. At the end of the 15th c. the main new development was the introduction of some new forms, usually ceramic copies of fashionable metallic vessels, for example ear-handled bowls or small jars with tubular body, high stem and prominent spout. The most highlighted new technological development of that period is the appearance of the blue-decorated ceramic, with decoration patterns strongly related to lustre pottery from Valencia.

As part of a large program designed to give a fuller picture of tin-glaze ceramic production in Spain (Molera et al. 2001; Pérez-Arantegui, 2002, 2004), the research was focused on the chemical characterisation and study of the ceramic technology of tin-glazed pottery produced in Teruel since the 13th c. to the 16th c. AD. This period was chosen for historical reasons, because in the 16th c. finished the presence of Islamic (Hispano-Moresque) people in Spain, always related to pottery production in Aragon.

Nearly one hundred fragments were selected for this study from the collections of the Museum of Teruel. Most of them are tin-glazed ceramics, but some samples of transparent-glazed and non-glazed pottery and wasters were also taken, in order to compare clay raw-materials. The selected tin-glazed fragments were decorated with only green, only brown or "green and brown" patterns and with blue designs. Therefore, through the characteristics of glazes and ceramic bodies, some technological features (such as thickness, whiteness, opacity, etc.) of the tin-glaze production in Teruel will be identified.

Experimental methods

Small fragments of glazed ceramics were cut perpendicular to the glaze-body interface with a diamond saw. Samples from some of the fragments were prepared as polished sections for examination by Scanning Electron Microscopy (SEM, JEOL JSM 6400), and optical microscopy. In addition, these sections were analysed using SEM with Energy Dispersive X-ray Analysis (EDXA, Link Analytical Systems, eXL-10); in each case, analyses were made scanning an area as large as possible (around 1000 μm^2, x2000 magnification), avoiding non-plastic inclusions. The distribution and morphology of the tin oxide crystals were studied on Backscattered Electron (BSE) images.

The chemical composition of ceramic bodies was determined by Inductively-Coupled-Plasma Atomic Emission Spectrometry (PERKIN ELMER, Plasma 40, ICP-AES). This analysis was undertaken on representative 50 mg sub-samples drilled from freshly fractured surfaces of the sherds. Sampling was carried out by drilling the fragments with a diamond drill (1 mm diameter) in the ceramic body core. Powdered samples were dried to constant weight at 110°C. Open-beaker dissolution in Teflon-tubes was used to prepare sample solutions. Samples were placed in a Teflon vessel and HNO_3–HCl/HF/HNO_3–$HClO_4$ were added in several steps with heating. After dissolution, samples were diluted to a final volume of 50 ml. Eight major elements (Al, Fe, Ca, Mg, K, Na, Ti and Mn) and two trace elements (Ba and Sr) were determined in every sample.

Results and Discussion

The chemical results obtained by EDXA show that all tin glazes used for decorating pottery in Teruel had high content of lead (Table 1). This fact was already observed in Islamic tin glazes and other medieval ceramics produced in the Iberian Peninsula (Molera 1996; Molera et al. 1999a, 2001; Pérez-Arantegui 1997; Pérez-Arantegui et al. 1999).

A statistical treatment (hierarchical clustering analysis) of the chemical composition data of tin glazes separates the samples in three main groups with different compositions (Fig. 3). Groups A and B include tin glazes decorated with green and brown designs. Group C corresponds to tin glazes decorated in blue. In Table 1, chemical composition of the three groups can be seen. Between groups A and B, main differences are lead content (higher in group A) and potassium proportion, this last element helps also to distinguish between the three groups, its highest percentage is in group C. Therefore three different compositions were used to prepare tin glazes in Teruel workshops during this period.

These tin glazes were the result of using a mixture of lead and alkali with sand or quartz and some clay (see aluminium content), but potters always used very pure sand and white clay, because iron content is near or below detection limits (< 0.5% FeO) in all glaze samples. Tin oxide content ranges from 4 to 12%, with enough quantity to produce opacity, but not very high in some cases.

Concerning tin-glaze microstructure, SEM observations show that all glazes have a similar thickness (between 125 and 150 μm). All of them were put on previously biscuited bodies and then fired again, as indicated by the very thin interaction layer (< 10 μm) observed between glaze and body (Fig. 4). However, there is also a third feature that leads us to distinguish two different types of glazes: the presence of non-plastic inclusions. The first type of tin glaze has a high number of inclusions (Fig. 4a), especially quartz, and nearly all samples from group A are included in this type. All samples from group C appear included in the second type, that with very few or no inclusions (Fig. 4b). The presence of quartz inclusions has been demonstrated to be characteristic of some Islamic productions of tin glazes, like Zaragoza, Granada and Pechina (Almeria) (Molera et al. 2001; Pérez-Arantegui 1997; Pérez-Arantegui et al. 1999), they are absent in Islamic tin glazes of Murcia and Denia (Molera et al. 2001).

Tin-oxide crystals are present in the glazes as opacifier, but cassiterite (SnO_2) crystals appear grouped in clusters and scattered with a high heterogeneity, with areas where many crystals are included and with other areas with no crystals (Fig. 5). In general, dimensions of tin oxide crystals are between 1 and 2 μm, so they are bigger than cassiterite in Islamic tin glazes (Molera et al. 2001), and these dimensions can be related to the firing process

Table 1: Average chemical composition of the three different groups (A, B and C) observed in tin glazes, and transparent glazes produced in Teruel (expressed in weight %) (in italic, standard deviation data).

GROUP		Al_2O_3	SiO_2	K_2O	CaO	SnO_2	PbO
A	(n=26)	4.11	41.7	1.61	0.63	8.34	43.2
	s	*0.87*	*2.39*	*0.44*	*0.33*	*2.88*	*3.36*
B	(n=12)	5.59	48.2	2.66	0.90	6.02	35.9
	s	*0.98*	*2.34*	*0.47*	*0.38*	*1.41*	*1.93*
C	(n=7)	4.50	47.4	4.63	1.63	4.88	36.4
	s	*1.20*	*2.33*	*0.38*	*0.45*	*1.34*	*1.93*
TRANSPARENT	(n=3)	5.50	41.8	1.30	1.44	—	45.5
GLAZES	*s*	*0.04*	*1.53*	*0.20*	*0.41*		*2.53*

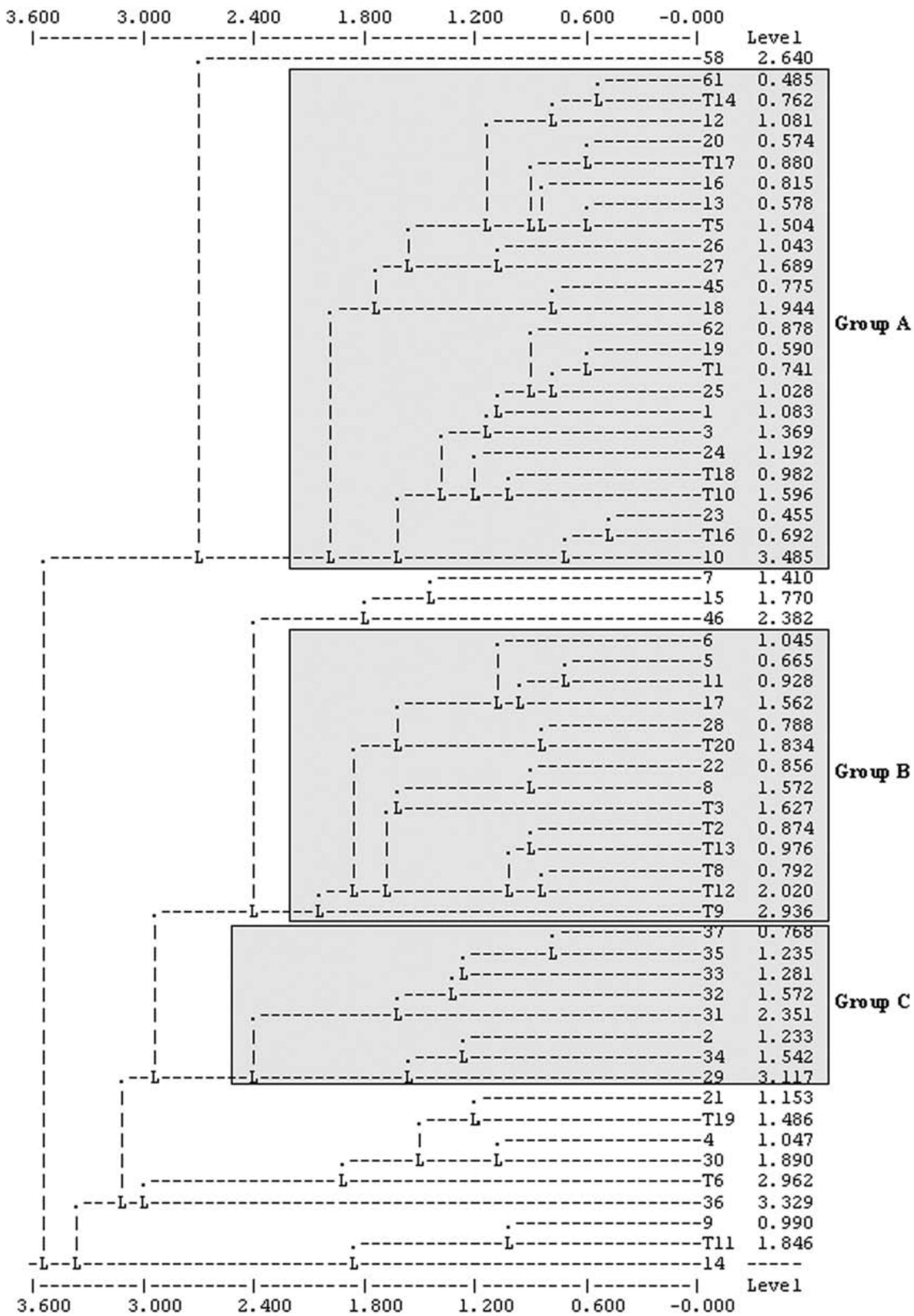

Figure 3: Hierarchical clustering analysis of tin-glaze chemical composition data.

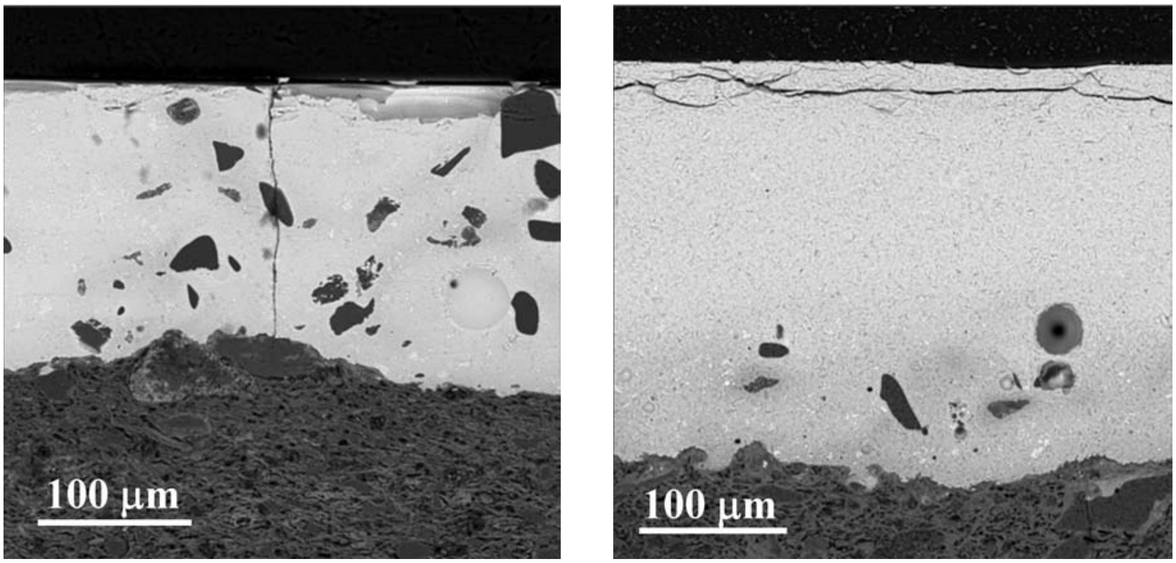

Figure 4: Scanning electron microscopy (SEM-BSE) images of tin glazes. a) Heterogeneous microstructure with many non-plastic inclusions. b) Homogeneous microstructure with no inclusions.

(Molera et al. 1999b). Even in some cases, big fragments of tin oxide can be found in the glaze, with angular forms, so they could come from ground cassiterite added to the glaze. This fact is especially observed in samples from group C, the blue-decorated tin glazes.

On tin glazes decorated in "green and brown", copper was used in green designs and manganese for black decorations as colouring elements. However, in the case of ceramics with only black-brown designs, a mixture of manganese and copper was always found in the analysis of the decorating lines. This combination (Cu+Mn) could come from the minerals used to prepare the raw pigments.

Concerning blue decorations, cobalt dissolved into the glaze is the element responsible for the colour. Even a small quantity of cobalt (< 0.6% CoO) is enough to produce blue colour in the glaze. When blue-decorated tin-glaze cross sections were studied by optical microscopy, a dark-blue layer between body and glaze was observed in many samples (Fig. 6). This layer can be also seen by SEM, with a high content of iron, probably related to the mineralogy of the raw materials used to produce cobalt pigments. This cobalt distribution is very different from others observed in cobalt decorations on tin glazes where cobalt diffuses from the surface to the inner glaze (Pérez-Arantegui et al. 1996). Therefore these fragments could be an example of under-glaze decoration, because the quantity of cobalt that arrives at the surface by diffusion is enough to produce the blue

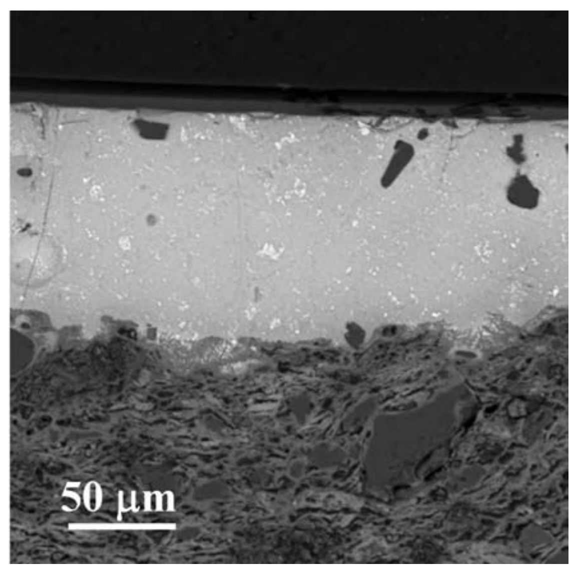

Figure 5: SEM-BSE image showing cassiterite (SnO_2) crystals.

colour in the glaze surface. Under-glaze cobalt decoration has been also observed in the ceramic production from the Valencian area dated to the 14th and 15th centuries AD (Roldan et al. 2004).

To study whether there are similarities or differences among glazes produced in Teruel, some fragments covered with transparent glazes were also studied by SEM. Main differences are the homogeneity of glazes (with no presence of inclusions) and

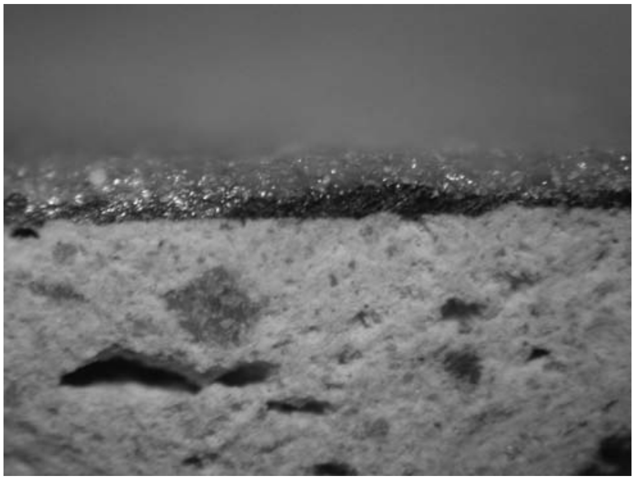

Figure 6: Cross section of a tin glaze decorated in blue (optical microscopy).

the fact that transparent glazes were always put on raw bodies and then fired. However the chemical composition of coloured glazes is similar to that of tin glazes (see Table 1).

In order to know the chemical compositions of ceramic bodies used for tin-glazed pottery, body samples were analysed by ICP-AES. Analytical results are shown in Table 2. A statistical treatment (hierarchical clustering analysis) of these data allowed us to classify the body composition in several groups. For tin-glazed ceramics two completely different types of clay bodies were used, they are especially distinguished by the calcium proportion. The first one includes all samples decorated with green and brown designs (tin-glaze groups A and B), and it is a less-calcareous clay group (7.4 wt% CaO). These bodies have a very red colour, the typical colour of Teruel pottery until today. The second type corresponds to clay bodies of fragments decorated in blue (tin-glaze group C), with calcareous clay (13.5 wt% CaO) and a white-buff colour due to the higher quantity of calcium and the consequent dissolution of the iron oxides (Molera et al. 1998). Therefore, potters from Teruel used completely different clay for ceramics decorated in blue, and at the same time they continued to use the other red clay for green and brown decorated pottery. This tradition of using calcareous clays for ceramic bodies coated with tin glaze was already noted in other Islamic and Hispano-Moresque workshops in Spain (Lapuente and Pérez-Arantegui 1999; Molera et al. 1996), due to the facility for opacifying a cream body.

A non-calcareous clay was also used but only for making cooking pots (see Table 2). This special clay used for cooking pots is also documented in other workshops and periods (Lapuente and Pérez-Arantegui 1999; Molera et al. 1996). In this case, a completely different ceramic tradition was followed for cooking pots than for tin-glazed pottery, because they were coated with transparent glazes with a higher lead content (55.7 wt% PbO).

Conclusions

As conclusions, we can say that potters in Teruel used two different clays to make tin-glazed pottery: one less-calcareous for green and brown decorated ceramics, and another calcareous clay for blue decorated objects. The second one was introduced at the same time as blue decorations (by the end of the 15th century), but this new body composition did not result in the disappearance of the other less-calcareous clay that is still used by potters in Teruel.

Tin-glazed objects were coated with glazes that have three different compositions: types A and B correspond to ceramics decorated in green and brown colours and type C was used in tin glazes decorated in blue. Two textures were distinguished with many non-plastic inclusions (especially tin

Table 2: Average chemical composition of the different groups observed in ceramic bodies for tin glazed pottery produced in Teruel, and the clay used in cooking pots (expressed in weight %) (Ba and St are expressed in ppm, standard deviation data in italic).

BODIES	Na_2O	MgO	Al_2O_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Ba	Sr
Less calcareous clays	0.20	1.49	15.7	3.60	7.44	0.53	0.028	4.69	433	131
s (n = 35)	*0.07*	*0.13*	*1.42*	*0.22*	*1.00*	*0.04*	*0.009*	*0.50*	*42*	*37*
Calcareous clays	0.47	1.43	16.1	2.66	13.5	0.64	0.023	4.41	428	207
s (n = 7)	*0.05*	*0.19*	*1.86*	*0.45*	*2.21*	*0.07*	*0.009*	*0.58*	*88*	*47*
Non-calcareous clays	0.24	1.17	17.7	3.07	3.00	0.69	0.031	5.84	409	90
s (n = 3)	*0.01*	*0.10*	*0.96*	*0.29*	*1.19*	*0.06*	*0.007*	*1.20*	*20*	*5*

glazes from group A) and no inclusions (tin glazes from group C). Therefore three different tin-glaze recipes were used by potters: two of them were firstly used at the same time and continued, and the third one was introduced later with different proportion of fluxes (PbO and K_2O).

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Notes

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Beads beyond number: faience from the 'Isis Tomb' at Vulci, Italy

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Abstract

Faience beads in several colours, along with many other artefacts including small fragments of yellow and blue glass, were recovered during the nineteenth century from the Etruscan Isis Tomb at Vulci. Fragments of glass and some of the beads, selected to represent the full range of colours, have been observed using a binocular microscope and analysed in a scanning electron microscope equipped with an energy-dispersive X-ray analyser. The observations show that the raw materials and recipes and also the techniques of manufacture of the faience beads are consistent with contemporary production in Egypt. This interpretation is reinforced by the presence in the tomb of other artefacts with Egyptian affinities.

Introduction

The Etruscan civilisation of west central Italy (Fig. 1) was a loose alliance of city states that had grown up out of the early Iron Age culture of Etruria, during the ninth and eighth centuries BC. The Etruscans enjoyed rich natural mineral resources and benefited also from their central position in an extensive trading network with contemporary civilisations, including the Greeks, Phoenicians and Egyptians. The high point of Etruscan civilisation was reached in the sixth century BC but it declined thereafter in the face of assaults by the Greeks, Gauls and Romans. The last of the independent Etruscan cities fell to the Romans in 264 BC and by the first century BC, the Romans had effectively assimilated Etruscan civilisation (for extended accounts of Etruscan civilisation and its origins see, for example, Briquel 2000 and Haynes 2000; for a summary see Swaddling 2002).

The so-called 'Isis Tomb' in the Polledrara Cemetery at Vulci was discovered in 1839 on the estate of Lucien Bonaparte, Prince of Canino (Haynes 1977, 1991, 2000: 154–9). Lucien was the brother of Napoleon Bonaparte and had been granted the estate near Vulci, to the north-west of Rome, by the Pope. The tomb owes its name to a hammered bronze statue found in the tomb and thought at one time to depict the Egyptian

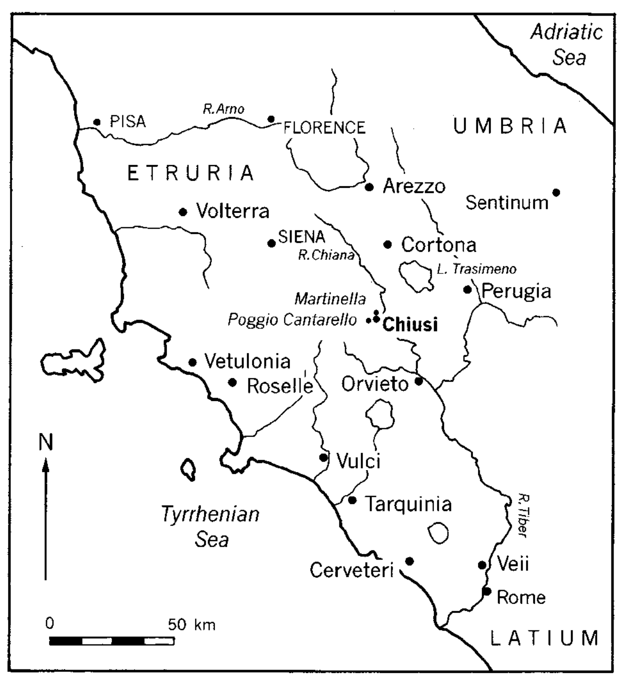

Figure 1: Map of Etruria indicating the location of Vulci (after Swaddling 2002).

goddess, Isis. This bust, almost 40 cm high, is now thought to be a representation of a native Etruscan fertility goddess or priestess and is of considerable interest as one of the earliest large-scale Etruscan bronze figures to have survived (Haynes 1991). Despite this, the name 'Isis Tomb' has remained.

Once opened, the Isis Tomb, like others on the estate, was emptied of its contents and then filled in; no plan or inventory was made and only items of monetary value were kept. In the process much pottery was discarded. The tomb contained the burial of a man and perhaps also that of a woman, and a particularly rich assemblage of antiquities. In 1844, Lucien Bonaparte's widow, Jouberthou, sold a collection of objects said to have been recovered from the tomb; in 1850 sixty of these were sold on to the British Museum by Dr. Emil Braun. The majority have been dated to c. 625–550 BC. Although all of these artefacts are thought to have come from Vulci, it is not certain that all originated from the Isis Tomb.

There is a further possible complication concerning the origin of these artefacts. Many of the finds from the Isis Tomb were exhibited in a special 'Egyptian cabinet' at Lucien Bonaparte's villa at Musignano, near Vulci. It is thought that some of these artefacts may have been brought from Egypt by Lucien Bonaparte, so that they could be relatively modern imports (Haynes 1977). However, some of the faience beads were found attached to the corroded metal of an Etruscan bronze incense burner in the Isis Tomb collection, securing their Etruscan archaeological context.

As well as the bronze statue, the items said to come from the tomb include others of more definite Egyptian affinity, including a pair of pale blue faience flasks (see Swaddling 2000 for a description and illustration of one of these flasks). The hieroglyphic inscriptions on the shoulders of one of these flasks are an expression of greetings to the owner. Flasks like this were used in rituals associated with the Egyptian New Year, which coincided with the beginning of the inundation caused by the great annual flood of the Nile in late summer. Also amongst the finds attributed to the Isis Tomb is a huge number of beads and associated fragmentary material (British Museum Reg. No. 1850.02-27.66). It is thought that the beads were associated with the interment, and that originally they would have been threaded together to form a shroud. Using a process of sample counting and weighing, the number of beads has been estimated to be in the region of 33,000 (Judith Swaddling, *pers. comm.*).

The textural examination and chemical analysis of these beads form the main focus of this short paper. The investigation described here was carried out some years ago under Michael Tite's guidance, and was one of my earliest introductions to the application of scientific techniques to the study of archaeological materials. I am pleased to have the opportunity to offer it for publication in this Festschrift.

Samples

The overwhelming majority of the beads (Fig. 2) are c. 3–5 mm in diameter. They had been divided into four groups on the basis of colour and, as noted above, the approximate number in each group estimated by weighing: turquoise c. 21,000; white c. 6,000; green c. 4,000 and pink c. 2,000. In addition, there is a group of about 90 smaller beads (c. 2-3 mm diameter) which include a similar range of colours, though excluding turquoise and with the addition of black. Some of the larger beads had apparently been joined together in pairs (about 90 pairs), and a single example of a large green bead, with the central hole apparently infilled to produce an "eye", was also made available for examination. Finally, various samples of materials that had been found associated with the beads were examined. These included very small (c. 1–2 mm), non-diagnostic fragments of translucent, pale blue and pale yellow glasses, and other fragmentary material. A summary of the material examined is given in Table 1.

Analysis

Examples of beads representing each of the different colours were selected for examination and analysis. In some cases it was noted that there was significant

Table 1: Summary of samples examined

Laboratory Number	**Description**
29023P	Pale green 'eye bead'
29022R	'Double beads' (turquoise)
28534W	Fragment of pale blue glass
29024Y	Fragment of yellow glass
29066P	Fragmentary material
29067Y	Fragmentary material
28535U	Small bead (black)
28548V	Blue-green bead (green)
28546Z	Apple green bead (green)
28545Q	Pink bead (pink)
28549T	Turquoise bead (turquoise)
28551U	White bead (white)
28552S	Buff bead (white)

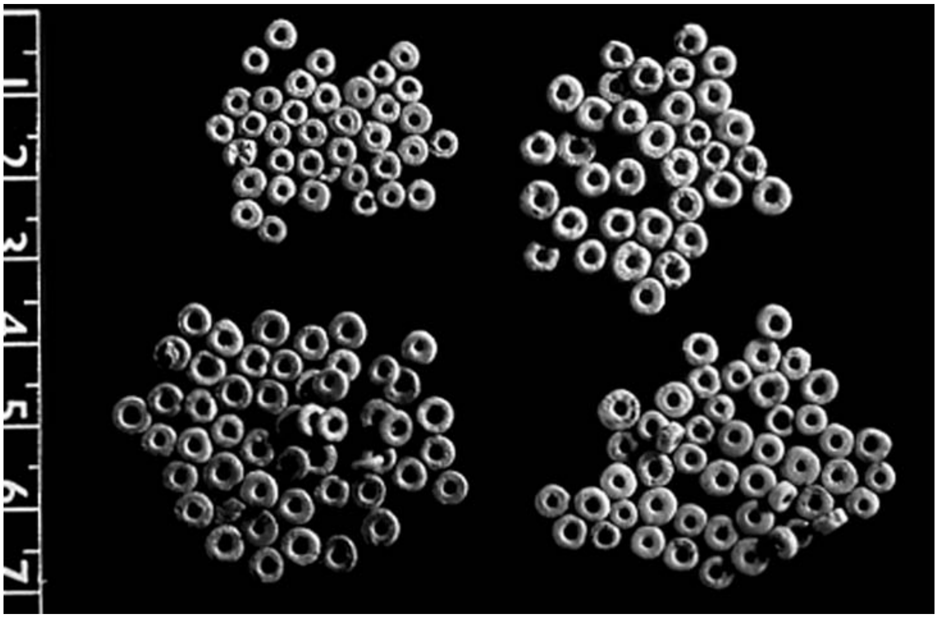

Figure 2: Beads from the Isis Tomb, Vulci, showing colours of the 'large' beads. Clockwise from top left, 'white' (buff), turquoise, pink, green; the scale bar is in cm.

variation in colour between beads classed as a single colour, especially those described as 'green' or 'white'. In these instances two beads of each colour were examined, as indicated in Table 1. Each bead was broken into two pieces. One part was mounted in resin (Araldite resin MY753, hardener HY951) and polished to a 1 μm finish using diamond pastes, so that cross-sections through the bead could be observed. After carbon coating, these samples were examined in a scanning electron microscope (SEM; JEOL JSM-840), equipped with an energy-dispersive X-ray analysis system (EDXA; Oxford Instruments (Link Analytical) 860–500) for elemental analysis. The accuracy and precision of these analyses was typically in the region of ±5–10% for major elements, increasing to ±20–30% for minor elements; limits of detection were typically 0.1–0.2%. The unmounted fragments were examined using a binocular microscope (Leica). Small fragments of the blue and yellow glasses were prepared in a similar manner. The 'double beads' and the 'eye' bead were examined under the binocular microscope, but were not prepared for analysis in the SEM.

Results and Interpretation

'Double beads' and 'eye bead'

Observation of several examples of apparently double, turquoise beads (Laboratory No. 29022R) indicated that in the majority of cases the two beads forming the pair are cemented together by what appear to be limonitic (hydrated iron oxide) corrosion products. In one instance, however, the beads were held together by a continuous layer of glaze. It is thought that this is likely to represent an accident of production rather than an intentional result, but deliberate production (or intentional selection and use of accidentally-produced double beads) cannot be excluded.

Examination of the pale green 'eye bead' (29023P) using a binocular microscope showed that the apparent eye effect was probably a fortuitous result of the attachment of iron-rich limonitic corrosion products. Similar limonitic material was noted amongst fragmentary material that had been separated from the beads when they were sorted by size and colour.

Blue and yellow glass

EDX analyses of fragments of the pale blue (28534W) and pale yellow (29024Y) glasses are given in Table 2. The two glasses are very similar in composition: both contain high levels of soda and low levels of potash and magnesia. The main difference between the two glasses lies in the presence of a small proportion of copper oxide in the blue glass, presumably added deliberately as the blue colorant. The pale yellow colour of the other glass is probably attributable mainly to the small amounts of iron. Thus it would

Table 2: EDX analyses of blue and yellow glasses

	Blue glass 28534W	**Yellow Glass 29024Y**
SiO_2	67.9	68.7
Al_2O_3	0.4	[0.5]
FeO	0.4	0.3
MnO	nd	nd
MgO	[0.5]	[0.4]
CaO	8.2	7.8
Na_2O	19.2	20.1
K_2O	0.2	[0.1]
P_2O_5	nd	nd
Sb_2O_3	nd	nd
CuO	1.6	nd
PbO	nd	nd
CoO	nd	nd
Cl	1.1	1.3
S	0.3	[0.2]
Total	100.2	99.6
n	2	3

nd: not detected; [ ]: below detection

seem that the two coloured glasses were made to the same basic glass recipe, their compositions indicating the use of natron, rather than plant ash, as the source of alkaline flux. It was noted that both glasses have distinct weathered layers (blue glass c. 30 μm thick; yellow glass c. 100 μm). Analysis of the weathered layers returned low totals and showed them to be heavily depleted in sodium.

Beads

It had been suggested that some of the darker, more buff coloured, 'white' beads may have been made from bone or ivory, but optical microscopy, chemical analysis and observation of textural features in the SEM (see for example Fig. 7) showed that 'white' beads of all shades are of faience. The EDX analyses for the differently coloured beads are summarised in Table 3. In each case analyses of the glaze and body were recorded from areas, selected to provide an estimate of the overall 'bulk' chemistry of the glaze or body. In addition, analyses were made at higher magnifications of areas selected to include only the interstitial glassy phase from the cores of some beads (see Table 3 for details). For convenience, the beads have been divided into three groups on the basis of

Table 3: Analyses of the beads

		SiO_2	CaO	Na_2O	K_2O	Al_2O_3	MgO	FeO	CuO	MnO	PbO	Sb_2O_3	CoO	Cl	SO_2	P_2O_5	Total	n
Group 1																		
Black	**Core**	94.7	0.6	nd	(0.1)	nd	nd	0.9	nd	2.8	nd	nd	nd	nd	nd	(0.5)	71.9	2
(28535 U)	**Glaze**	87.5	1.6	(0.4)	(0.3)	(0.7)	(0.3)	(0.8)	0.6	7.1	(0.5)	nd	nd	0.9	(0.2)	(0.4)	85.5	7
Green	**Core**	95.8	nd	nd	nd	nd	nd	1.4	1.1	nd	nd	nd	nd	nd	nd	(0.4)	75.5	2
(28548 V)	**Glaze**	87.6	1.0	nd	nd	(0.4)	nd	0.4	8.9	nd	nd	nd	0.4	0.5	(0.2)	(0.4)	92.4	2
Group 2																		
Pink	**Core**	91.4	0.8	1.0	0.2	0.3	0.4	5.2	nd	nd	nd	na	nd	0.1	nd	nd	76.6	1
(28545 Q)	**Glaze**	88.6	5.1	(0.4)	nd	(0.3)	(0.3)	4.4	nd	nd	nd	na	nd	1.3	nd	nd	86.1	3
	Glass	79.3	2.9	2.4	0.9	1.2	nd	11.7	nd	nd	nd	nd	nd	0.5	0.4	nd	87.9	
Turquoise	**Core**	93.6	0.4	0.5	0.2	(0.3)	nd	1.6	2.2	nd	nd	nd	(0.4)	(0.1)	nd	(0.5)	-	2
(28549 T)	**Glaze**	84.8	3.0	(0.6)	nd	(0.3)	nd	0.3	9.8	nd	nd	nd	0.4	0.4	(0.3)	(0.3)	89.7	2
	Glass	71.6	0.9	8.9	3.8	1.4	(0.2)	2.8	6.1	0.7	(0.4)	nd	0.6	0.6	(0.3)	nd	94.5	2
Group 3																		
Off-white	**Core**	98.6	nd	nd	nd	nd	nd	0.4	nd	nd	0.8	na	nd	nd	nd	nd	-	1
(28551U)	**Glaze**	88.4	(1.5)	(0.3)	nd	nd	nd	nd	nd	nd	9.1	nd	nd	0.9	nd	(0.5)	90.0	2
	Glass	84.1	0.9	nd	(0.4)	(1.2)	0.3	2.2	nd	nd	7.5	1.1	nd	0.8	(0.5)	(0.7)	87.7	4
Dark buff	**Core**	97.1	nd	nd	nd	nd	nd	0.4	nd	nd	1.3	nd	nd	0.2	nd	nd	72.8	1
(28552S)	**Glass**	82.5	3.4	nd	(0.4)	1.1	0.7	2.6	nd	nd	7.5	(0.7)	nd	0.9	nd	nd	87.7	3
Pale green	**Core**	97.5	nd	nd	nd	nd	nd	(0.3)	(0.6)	nd	0.6	nd	nd	nd	nd	0.5	70.2	2
(28546Z)	**Glaze**	85.2	4.5	nd	nd	nd	(0.2)	nd	3.3	nd	4.5	nd	nd	1.7	nd	(0.3)	89.3	2
	Glass	83.3	1.6	(0.3)	0.8	2.0	0.4	2.8	2.4	nd	4.8	nd	nd	0.9	(0.4)	nd	87.4	3

na = not analysed; nd = not detected; () = below detection in one or more analyses

Table 4: Summary of colorants and manufacturing techniques

Colour	Pigment	Technique of manufacture of faience (group)
Glasses		
Yellow	iron (probably accidental)	-
Blue	copper	-
Faience		
Black	manganese	Cementation (1)
Green (blue-green)	copper + cobalt	Cementation (1)
Turquoise	copper + cobalt	Efflorescence (2)
Pink	iron	Efflorescence (2)
Green (pale green)	copper + lead antimonate	Efflorescence (3)
White (originally yellow?)	lead antimonate	Efflorescence (3)

the textural observations and analytical results. A summary of the pigments used to make the variously coloured beads is given in Table 4.

Group 1

This group includes the small black beads and also those green beads which are of a blue-green colour. In the SEM they are characterised by a relatively restricted glaze layer (< 50 μm thick) and a glaze/core interaction layer c. 100 μm thick (terminology of Tite and Bimson 1986). There is no significant vitrification in the core of the beads (Figs. 3 and 4). In the case of the black beads (e.g. 28535U) the colorant in the glaze appears to have been a manganese-rich pigment; manganese is present in the glaze and small manganese-rich particles (up to c. 20–30 μm) can be observed throughout the body of the bead (Fig. 3). Only traces (<1%) of alkali were detected in the glaze and glaze/core interaction layers but original levels would probably have been in the region of 15%, the loss of alkali being a result of weathering and hydration of the glassy phase during burial. This phenomenon is thought to be responsible for the low analytical total for the glaze on the black bead (see Table 3, 28535U).

The glaze on the blue-green beads in this group (e.g. 28548V) was coloured by copper and a small amount of cobalt. Particles of rather variable composition but typically containing Mn, Fe and Ni in addition to Cu and Co, and found scattered throughout the body of the bead may provide evidence of the nature of the original pigment but this has not been pursued here. The level of alkali in the glaze and glaze/core interaction layers is low (<1%) but again this is probably a result of post-depositional weathering, and it is thought that the glassy phase originally would have contained about 15% total alkali.

Group 2

Included in this group are the pink (e.g. 28545Q) and bright turquoise (e.g. 28549T) beads. In the SEM (Figs. 5 and 6), both are seen to have glaze layers up to about 50 μm thick with relatively thick (200–300 μm) glaze/core interaction layers. It was also noted that there is fairly extensive development of a glassy phase in the cores of the beads.

The pink and turquoise colours of the glazes on these beads were produced by the use of iron and copper plus cobalt respectively (see Table 3). As with the beads of Group 1 it appears that the pigmenting material was mixed with the crushed quartz before the bead was made, for iron-rich or copper-rich particles occur in the bodies of the beads. Both the pink and turquoise beads contain significant amounts of alkali in the glass in the core and in the glass/core interface region. However, the glaze layer itself has very low alkali levels, presumably as a result of weathering.

Group 3

This group comprises the remainder of the beads, i.e. all of the 'white' beads (e.g. 28551U, 28552S) and the majority of the 'green' beads (i.e. those of a pale apple green colour, e.g. 28546Z, rather than the more blue-green beads of Group 1). These beads have glaze layers up to c. 50 μm thick, relatively thick (up to c. 400 μm) glaze/core interaction layers, and fairly extensive development of a glass phase in the cores of the beads (Figs. 7 and 8).

A characteristic feature of these beads is the presence of c. 5–10% lead oxide in the glaze and in the glass phase of the core and glaze/core interaction layer. The lead was almost certainly introduced by the use of a lead antimonate pigment, particles of which occur in the glaze and interstitial glass phase of both the white and green beads.

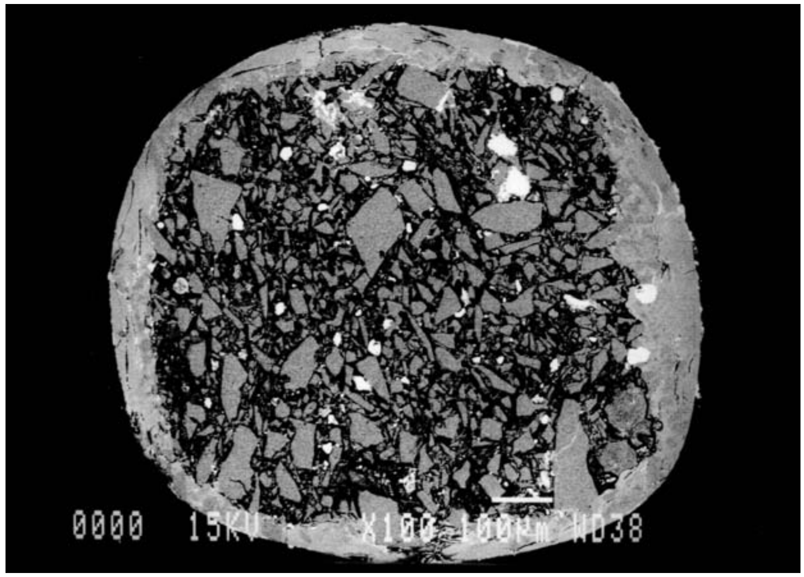

Figure 3: SEM photomicrograph of cross-section of black bead (28535U). The bright particles are rich in manganese.

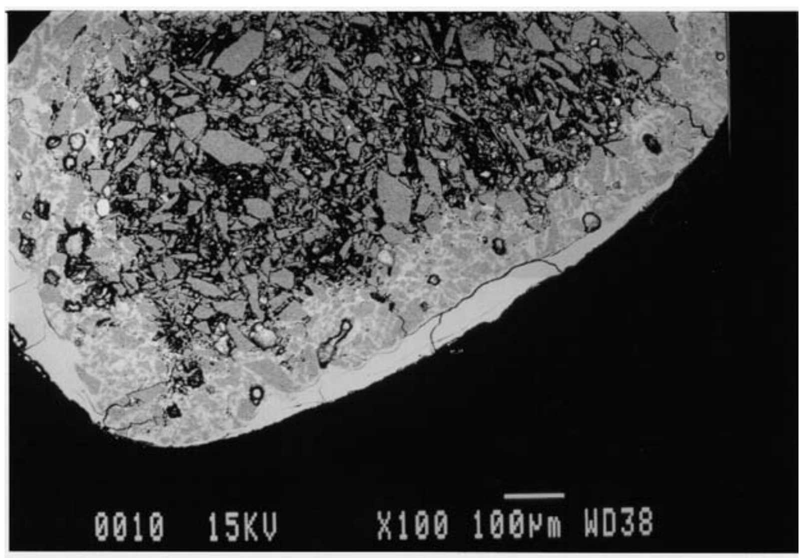

Figure 4: SEM photomicrograph of cross-section of green (blue-green) bead (28548V).

The apparent use of lead antimonate for the white beads is surprising. The colour normally associated with lead antimonate is yellow and, although opaque white glass was made by the use of calcium antimonate, white faience was typically produced by the application of a clear colourless glaze that exposed the white, crushed quartz core (Kaczmarczyk and Hedges 1983; Shortland 2002). It was observed that on fracture surfaces the vitrified bodies of the 'white' beads present a pale yellow colour when viewed under the binocular microscope, and the beads may originally have been a brighter yellow, the loss of colour being a result of weathering. However, Kaczmarczyk and Hedges (1983) noted that overfiring can lead to loss of the yellow colour in faience. The sensitivity of the lead antimonate pigment to high temperature was noted also by Shortland (2002: 525) in his practical experiments to replicate the use of lead antimonate to produce yellow and green glasses. He observed that if the lead antimonate is mixed with glass at too high a temperature it may dissolve, producing a creamy coloured, rather than yellow,

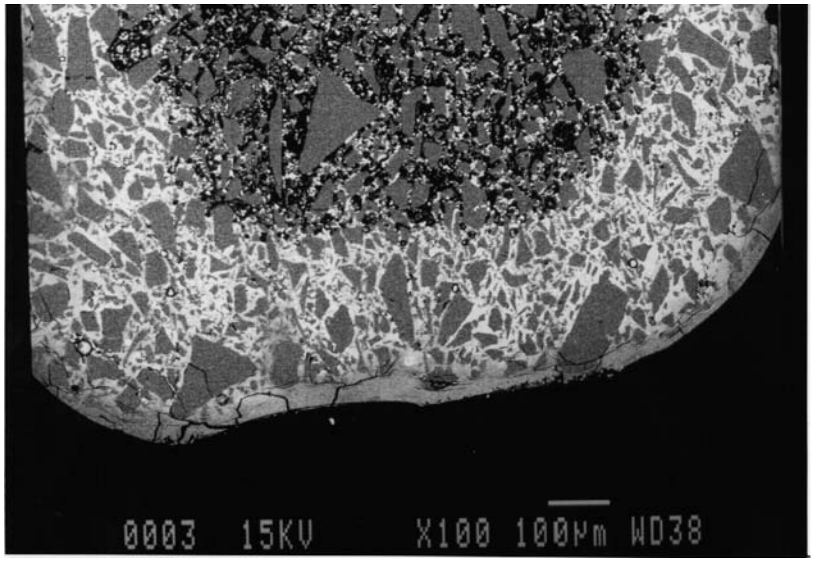

Figure 5: SEM photomicrograph of cross-section of pink bead (28545Q).

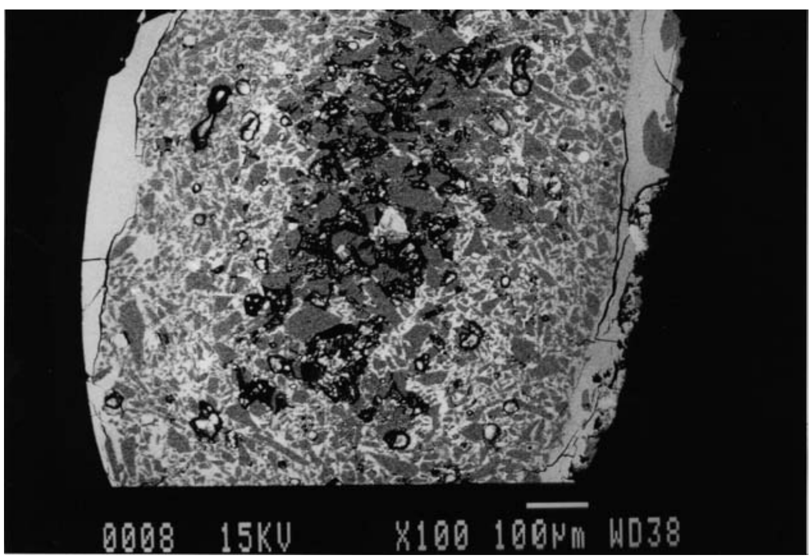

Figure 6: SEM photomicrograph of cross-section of turquoise-blue bead (28549T).

glass. Thus, it is possible that the beads from the Isis Tomb were never the strong yellow colour normally associated with glasses pigmented with lead antimonate.

The colour of the pale green beads was produced by the combination of yellow lead antimonate and the copper-blue of the glassy matrix.

The levels of alkali in the glaze and glass phase of the core and glaze/core interaction layer are low (<1%) in both the white and green beads. As for the beads of other colours that have been discussed already, these low levels of alkali are thought to be a result of weathering, the original total alkali content having been c. 15%. Nevertheless, the almost total loss of alkali, even from the core, is rather surprising in view of the well preserved appearance of the beads and the relatively thick glaze plus glaze/core interaction layers.

Techniques of manufacture of the faience beads

Three basic methods for the manufacture of glazed faience objects have been recognised, as discussed

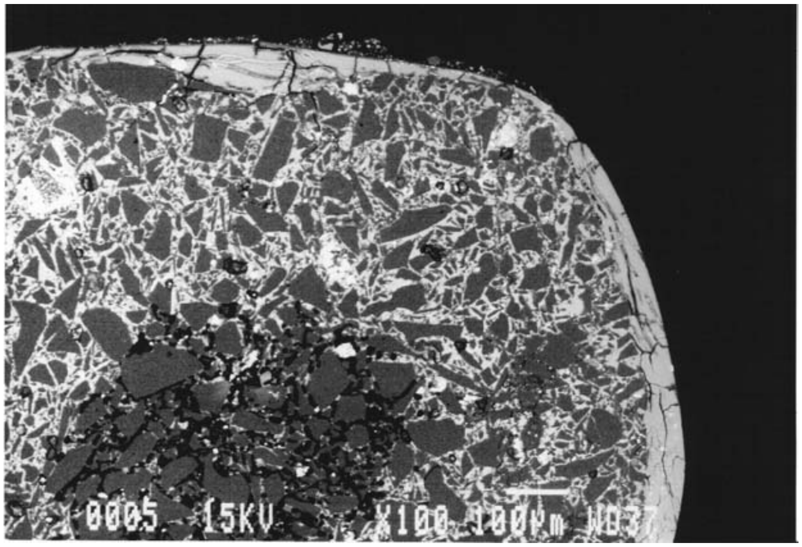

Figure 7: SEM photomicrograph of cross-section of 'white' bead (28551U).

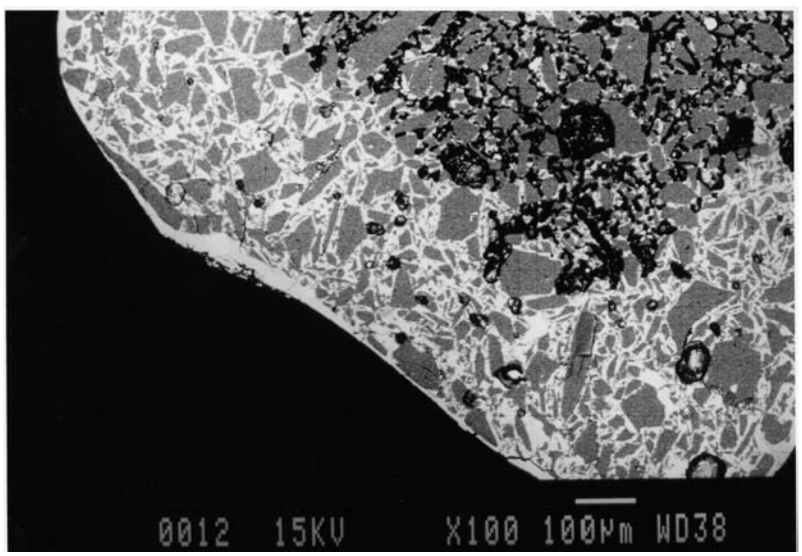

Figure 8: SEM photomicrograph of cross-section of apple green bead (28546Z).

for instance by Vandiver and Kingery (1986) and Tite et al. (1983): (i) direct application of the glazing mixture to the surface of the ground quartz body; (ii) efflorescence self-glazing in which the glazing components were mixed with the moist quartz body and were then carried to the surface during drying; (iii) cementation self-glazing in which the object was embedded in the glazing mixture and fired. Tite and Bimson (1986) discussed criteria for the recognition of these various production techniques (for turquoise-blue faience) from textural features observed in the SEM. More recently, some of the difficulties and ambiguities in interpreting faience technology from microstructures were discussed by Vandiver (1998), who commented also on the particular difficulties associated with the examination of weathered materials such as those described in this study. Despite these uncertainties, it is hoped that the present study has provided sufficient information to be able to go at least some way towards characterising the raw materials and techniques used to make the 'Etruscan' beads from the Isis Tomb. Evidence from excavations (see for example the factory evidence reviewed by Nicholson and Peltenburg 2000), including recent re-investigation of an area of kilns identified originally by Petrie (Nicholson 2001, 2002), may

lead to a greater understanding of the methods used to make Egyptian faience.

The black and blue-green beads of Group 1 are characterised by an absence of glass in the core and were probably produced by the cementation self-glazing method. It appears that the pigmenting agents (black: manganese; blue-green: copper plus cobalt; see Table 4) were mixed with the crushed quartz rather than being only in the cementation glazing mixture, as was usually the case when objects were made in this way.

The turquoise and pink beads of Group 2 contain glass in their cores suggesting that they were produced by the efflorescence method. In this technique, the pigmenting material (pink: iron; turquoise: copper plus cobalt), as well as the source of alkali, was mixed with the crushed quartz paste before it was used to make the beads.

The white, buff and green beads of Group 3 also have vitrified cores, suggesting that they too were made by the efflorescence method. These beads are distinguished from Group 2 by the use of lead antimonate as a colorant (white, probably originally yellow: lead antimonate; green: lead antimonate plus copper).

The glaze within the central hole of some beads from Groups 2 and 3 is thinner than the glaze on other surfaces of the bead (or even absent). This may have resulted from a reduced level of efflorescence within the hole compared with the exposed external surfaces (i.e. surfaces with a large surface to volume ratio, Vandiver 1998: 135–6 and table 4). It is possible also that the beads were 'threaded' onto some sort of 'rod' to support them during firing. This effect was not noted on the turquoise beads of Group 2, and the absence of any support marks on these bright turquoise beads suggests that during firing they were placed in an inert mixture which served mainly to separate individual beads and thus prevent them from fusing together.

Discussion and Conclusions

Plant ash, with relatively high levels of potash and magnesia, as well as soda, was the source of alkali for early Egyptian glasses (see, for example, Lilyquist and Brill 1993). The essentially pure soda source, natron, appears not to have been used widely until the eighth century BC (Henderson 2000a, b), although Schlick-Nolte and Werthmann (2003) have described vessel glass from a tenth century BC Egyptian context fluxed with natron, and Henderson (2001) has recorded examples from the second millennium BC. Nevertheless, the blue and yellow glasses from the Isis Tomb represent fairly early examples of the use of natron from a period when relatively few examples have been reported. The production of blue glass using copper and cobalt to modify an essentially colourless, basic glass recipe is typical for Egyptian glass (Shortland 2002). Certainly, the glass from the Isis Tomb is quite different from a group of pale blue, translucent Etruscan glasses analysed by Towle and Henderson (2002). These unusual glasses are characterised by a high level of potash (typically 15–20%) and very low soda (below detection by EDX analysis in an SEM); they are coloured by cobalt, with only very low (<0.1% CuO) copper. Towle and Henderson suggested tentatively that the identification of this group of potash-glass beads may hint at a distinct Etruscan glass-making tradition but the fragments from the Isis Tomb clearly do not belong to the same tradition.

Because the faience beads are heavily weathered and most of the alkali metals have been lost, interpretation of the source of alkaline flux used in their manufacture is much less certain. However, the relatively high ratios of potash and magnesia to soda, preserved in glass from the cores of the Group 2 (pink and turquoise) beads may perhaps be interpreted tentatively as evidence for the use of plant ash, rather than natron.

There is no evidence that colours other than copper blue and manganese black were used for faience in Egypt before the invention of glass and their use in the manufacture of coloured glasses (see discussion in Shortland 2002; Kaczmarczyk and Hedges 1983). However, after the mid-Eighteenth Dynasty cobalt blue, lead antimonate yellow and other colorants were introduced to faience as well as to glass. The colorants and techniques of manufacture (summarised in Table 4) used for the variously coloured beads described here are typical of those attested for Egyptian faience (Kaczmarczyk and Hedges 1983).

Thus, it seems most probable that the beads and associated vitreous materials thought to have come from the late seventh to sixth century, Etruscan Isis Tomb were obtained originally from an Egyptian source. Certainly, this would be consistent with the extensive trading links enjoyed by the Etruscans with Egypt, and the evidence of the other artefacts with Egyptian affinities found in the tomb when it was opened in the nineteenth century. Beads very similar to those from the Isis Tomb were used to form a mosaic scarab beetle design on some Egyptian mummy coverings and a contemporary example is that of Takhebkhenem (British Museum, EA6692), found at Thebes and dated to the 26th Dynasty. This

perhaps suggests that the shroud from the Isis Tomb could have been brought to Etruria as a finished item.

The possibility of obtaining confirmatory analytical evidence for the Egyptian affinities of the faience beads is suggested by recent studies reported by Shortland and others (2000, 2002). This work has shown that lead isotope and trace element analysis may be useful in determining the source of the lead and antimony used to produce lead and calcium antimonate colorants used for glass and faience. Demonstration of a common source for the attested Egyptian examples and for the 'Etruscan' faience and glass colorants would support the inference that the grave goods from the Isis Tomb in the Polledrara cemetery at Vulci were manufactured in Egypt.

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Note

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Chapter 8

Egyptian blue in Greek painting between 2500 and 50 BC

I. Kakoulli[1]

Abstract

Blue is a colour of particular importance to painters, but naturally occurring blue pigments are uncommon, and are found only in limited areas. This might explain the scarce use of natural blue pigments in antiquity and the prevailing use of *Egyptian blue,* an artificial compound of calcium copper silicate. This term refers to a multicomponent pigment with the main constituent being a crystalline phase identical in formula to cuprorivaite mineral [$CaCuSi_4O_{10}$] found in association with glass and residual quartz. The inclusion of leaded glass found in the samples studied is a unique feature that chronologically agrees with the first occurrence of Ptolemaic leaded glazes and glazed faience. Investigations of the technology of Egyptian blue indicated that the particle size of the raw materials used during manufacture is of particular significance, as is the specific firing temperature employed. Of all the unique components found in all ancient samples, it appears that the fluxes and other minor elements present may be the most suitable for characterising Egyptian blue sources. Colour changes and deterioration of Egyptian blue were also observed. These changes included chemical weathering of Egyptian blue by dissolution of the glass phase.

Introduction

Painting was without doubt central to the culture of ancient Greece, and its study can therefore cast light upon many aspects of the social and technological structure of the period. The artists' palette consisted of a limited number of natural and synthetic pigments and colorants. These were applied in *secco* directly on marble and stone surfaces or in *fresco* on plaster layers of varying stratigraphy (Kakoulli 1999). Dependably on their availability and cost, some of the pigments were more common than others. Among the primary colours used for painting of particular interest are the blue pigments and mainly Egyptian blue as it is the only artificially made pigment and the most widespread of all both chronologically and geographically. Studies of its composition and manufacturing process have cast light on ancient technologies and intercultural links within the ancient world.

Blue pigments in Greek painting

Egyptian blue is the dominant blue pigment of ancient Greek painting from the third millennium BC. Only four exceptions have been identified to date: glaucophane, a titaniferous copper oxide, azurite and lapis lazuli. Azurite, although not common in ancient Greek painting, seems to have been extensively used in Dynastic Egyptian painting together with cobalt blue, the latter not yet found in ancient Greek art (Lucas and Harris 1962: 361 and Riederer 1974: 102–109).

Egyptian blue was identified in Minoan and Mycenaean monumental paintings in Crete, at Keros and Mycenae, in Classical and Hellenistic paintings in Macedonia and other provinces of the empire such as Egypt, Israel and Cyprus (Kakoulli 2002 and 1999). It was also found in Etruscan tombs at Tarquinia and Cerveteri embellished with magnificent wall paintings that reflect not only the culture and funerary

customs of this ancient civilisation, but also the Archaic monumental Greek art that had reached the Etruscans via Magna Graecia, continuing a tradition lost in Greece by this date (Borrelli 1985 and 1994).

Glaucophane, – a blue-black amphibole ($Na_2Mg_3Al_2(Si_8O_{22})(OH_2)$ – seems to have been used only during the Minoan period in paintings at Thera and Crete as early as 3000 BC but disappeared from use after 1500 BC (Filippakis et al. 1976: 143–153; Heaton 1910; Duell and Gettens 1941–42; Profi et al. 1976: 34–39; Profi et al. 1977: 107–115; Profi et al. 1974: 105–112). Its limited chronological use may imply that the pigment was imported to Crete from Thera, since the discontinuation of its use coincides with the eruption of the volcano; there is a controversy about the date of the eruption of the volcano (Manning et al. 2006), although most scholars provide a date of about 1500 BC.

Scientific examination of the polychromy of the Parthenon marble sculptures and architectural elements (fifth century BC) carried out by M. Faraday in the second quarter of the nineteenth century (1837) revealed the presence of a titaniferous copper oxide and a blue copper carbonate (most likely azurite) applied with wax (Jenkins and Middleton 1988: 201). Azurite, a natural copper carbonate pigment ($Cu_3(CO_3)_2(OH)_2$ was also identified on a painted sarcophagus from Cyprus dated c. 750 BC and now at the Metropolitan Museum of Art, New York (E. Hendrix pers. comm.). Lapis lazuli, a natural and rare blue coloured pigment comprising mostly of the mineral lazurite $(Na,Ca)_8Al_6Si_6O_{24}(S,SO_4)$ was reported as the blue pigment used on the painted sarcophagus at Ayia Triadha (Immerwahr 1990: 13). No other occurrences of this pigment were found in Greek painting.

Blue pigments were used pure, mixed among each other, or in combination with other pigments. At Keros (2500 BC) pure Egyptian blue was found while at Knossos, different patterns were observed: those dated earlier than 1700 BC consisted mostly of glaucophane or mixtures of glaucophane and Egyptian blue (with the exception of three samples containing only Egyptian blue), whereas those later than 1500 BC consisted only of Egyptian blue (Heaton 1910; Duell and Gettens 1941–42; Profi et al. 1976: 34–39; Filippakis et al. 1976: 143–153). Samples from Thera (all dated earlier than 1500 BC) consisted of pure Egyptian blue, or pure glaucophane, or both mixed together (Filippakis et al. 1976, 143–153; Profi et al. 1977: 107–115). At Mycenae, Pylos and Tiryns, analytical data pointed out the use of a single blue pigment, identified as Egyptian blue with a high quantity of iron, owing to iron-containing clays in the samples (Filippakis et al. 1976; Profi et al. 1974: 105–112).

New observations

During the Hellenistic period, paint samples from Delos showed that Egyptian blue was applied over a dark grey intermediate layer (Fig. 1). A similar application was also found in two samples from Acre in Israel, whereas in the samples from Jericho, Egyptian blue was applied directly over the plaster layer. In one of the samples from Jericho, Egyptian blue particles were mixed with large particles of celadonite. In the samples from Tomb 'Ammoi A' in Cyprus, the pigment was applied pure over the plaster layer. Analyses indicated the presence of tin-rich alkali glass together with the Egyptian blue crystals and the quartz. Blue samples from Gabbari in Alexandria, Egypt had a similar composition and application to those from Cyprus, possibly being mixed with lime and applied directly over the white ground. Fragments from the ex-English Consulate area also in Alexandria, showed a variety of applications of the blue pigment. In the samples from this site, Egyptian blue was used mixed with calcium carbonate to form a light blue paint layer. Although the colour of the two paint layers was almost identical, microscopical examination of the polished sections indicated that the first sample consisted of fine grained blue crystals applied over a grey layer, whereas the second consisted of large crystals of Egyptian blue including aluminium-rich glass particles, applied directly over a white plaster layer.

Egyptian blue was also found in admixtures with green earth. These were identified in samples from Egypt, Israel and Cyprus in different hues from bluish green, to greenish blue. In Israel, this mixture was applied over a grey intermediate layer to enhance the colour (Kakoulli 2002 and In Press).

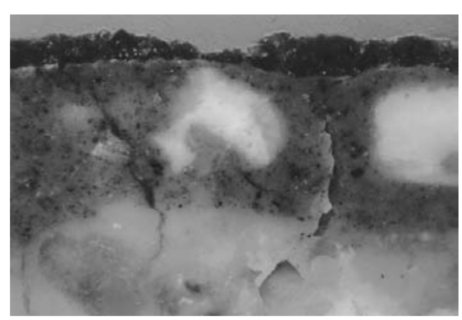
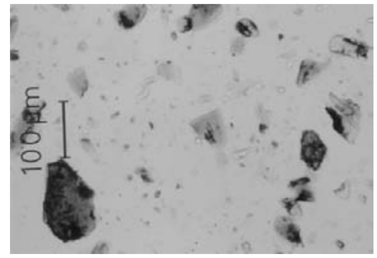
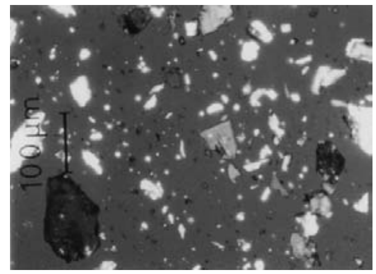


Figure 1: Thin section photomicrograph of a blue sample from a Hellenistic wall painting fragment from Delos photographed at 200x magnification. It shows from top to bottom: a blue paint layer consisted of Egyptian blue over a grey intermediate layer over plaster. [Photo: Kakoulli 1997]

Combined with an organic red colorant Egyptian blue was used to produce a purple colour (Kakoulli 2007 and In Press). In a sample from the ex-English Consulate in Alexandria, randomly oriented particles of Egyptian blue are mixed with a red lake (using calcium carbonate as the inorganic inert substrate). Both Vitruvius (VII, 14, 1 and 2) and Pliny (NH XXXV, 44) describe various substitutes for the purple colour (from shellfish). Pliny's description in particular — referring to the use of Egyptian blue (*caeruleum*) and a red colorant (*purpurissum*) — finds a close echo in the composite purple colour identified in the sample from Egypt.





Figures 2 and 3: Photomicrographs of Egyptian blue pigment from the painted marble throne at the Tomb of Eurydice, Macedonia, Greece. The particles of Egyptian blue were photographed at 200x magnification in plane polarised light (top) and with crossed polars respectively. [Photos: Kakoulli 1994]

Composition and chemical characteristics of Egyptian blue

Egyptian blue was the only blue pigment found in almost all ancient Greek paintings. Its crystal structure is identical to cuprorivaite, a rare natural mineral (Riederer 1974; Ulrich 1987). However, analysis of ancient material shows a variety of fabrics and compositions that distinguished it from cuprorivaite. This was due to the presence of other phases formed from the excess SiO_2, CaO, CuO and alkalis.

Egyptian blue is commonly composed of three distinct phases, each of which is associated with its manufacture. These are Egyptian blue crystals, glass, and residual quartz. In plane polarised light, the particles of the first phase display angular habit and a bluish colour; on rotation of the stage they show moderate pleochroism (Fig. 2). In crossed polars they are birefringent with high order interference colours (Fig. 3).

However, the three distinct phases of Egyptian blue described above are not always present; in some cases only cuprorivaite crystals and quartz particles maybe observed, as for example in one of the samples from a terracotta vessel in Delos. It seems that the absence of the glass phase relates to processes during its manufacture and preparation, especially sintering and grinding. Wollastonite or cassiterite may also be found in Egyptian blue pigment pellets.

In most Greek paintings the blue pigment had a dark blue colour, and consisted of large crystals whereas in only a few samples the pigment had a pale light blue colour with very finely ground particles. The main component of the pigment was always the crystalline calcium copper silicate phase, to which the glass and quartz phases adhere (Fig. 4).

Technical analysis of a few Hellenistic samples taken from a hoard of painter's raw materials in Delos showed a markedly high concentration of lead oxide in the glass phase (Kakoulli 1999). This observation is new to the published literature about Egyptian blue. Leaded glazes were introduced to Egypt during the Ptolemaic period (Minunno 1986: 345): could the introduction of lead oxide relate to this change in glass technology? Such a link would suggest an Egyptian centre of manufacture. Indeed, the discovery raises many new questions concerning the manufacture and trade of this pigment. Research is currently being carried out to identify the origin of lead; from data available so far, it seems that the lead may originated from bronze, the use of which is indicated by the concentration of lead in the bulk analysis of the matrix and the traces of arsenic and tin present in all three samples. High lead concentration was also identified in samples from Memphis suggesting the use of leaded bronze as the source for copper (Tite: personal communication). Whether the use of leaded bronze alters the properties of Egyptian blue needs further investigation.

All other paint samples from Delos containing Egyptian blue indicated the presence of only alkali glass; no traces of lead oxide were detected. Small quantities of tin were also identified in a small number of samples, suggesting the use of bronze as the source for the copper constituent.

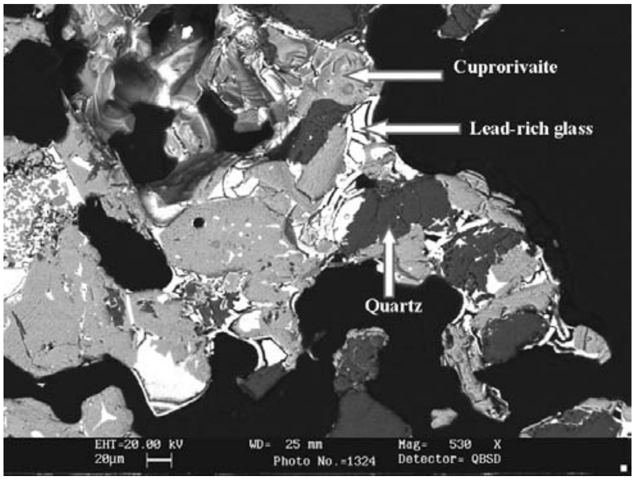


Figure 4: Back scattered electron photomicrograph showing a detail of Egyptian blue with leaded glass inclusions. The sample was taken from Delos, Greece. [Photo: Kakoulli 1997]

Manufacture of Egyptian blue

Ancient literary sources and recipes

Although Egyptian blue was used as early as the third millennium BC in Egypt and the Near East, the earliest written source referring to the material are the cuneiform texts from the library of Ashurbanipal (seventh century BC, but copies of original texts dating to the mid-late second millennium BC). The texts provide information on the making of coloured glass in Mesopotamia, in imitation of precious stones. It seems that Egyptian blue was produced as a simulation of lapis lazuli. In Akkadian two terms were used to describe "genuine" and "artificial" lapis lazuli, *kûru* and *adû (*von Saldern et al. 1988: 10).

The terms "fast bronze" and "fast copper", referring to a blue pigment — a lime silicate with high copper content (von Saldern et al. 1988: 77) — are mentioned in lists recording the tribute received from king Midas of the Phrygians, and by a ruler of Hattina (the Assyrian designation for the Amuq valley in northern Syria). This pigment could also refer to Egyptian blue (in adition to blue glass) produced in either Syria or Egypt and traded through Syria.

Supportive documentary evidence is presented by the Neo-Babylonian Uruk tablet, YO56 168, which is dated to 550 BC and in which many raw materials are listed alongside their worth in silver. "Lapis lazuli" is mentioned at a value of 36.2/3 silver shekels. The natural pigment was normally traded westward and not to Mesopotamia; since the price is very low for true lapis, the reference is likely to be to some substitute, either glass or Egyptian blue (von Saldern et al. 1988: 13).

In §8 of Tablet A (von Saldern et al. 1988: 41) *t*here is a description of the production of *uqnû merqu*. This probably corresponds to the manufacture of Egyptian blue:

> You keep a fire burning in the atûnu-kiln for seven days. For one mina of (good (?)) tersîtu-preparation (you take) three minas of tarabanu of addu quality, (ten) shekels of busu-glass of addu quality, five shekels of 'white stuff' from the sea wh(ich is made of (?)) coral, two shekels of anzahhu-glass, three shekels of er-erru-color, four shekels of 'male' red alum, five shekels of lêru-color, six shekels of 'white plant'. You mix (these) and grind them finely again. You collect (the powder) in a mold and out (of the kiln) will come (fine) lapis lazuli colored glass. (Postscript:) What does not become vitrified (?) enough you place (again) in the atûnu-kiln (and keep) the fire (burning) for (another) seven days.

In *De Lapidibus* (Theophrastus *On Stones) (*1956: 55), Caley and Richards mention a synthetic blue pigment which he calls *kyanos*, which was produced in Egypt and traded. "Kyanos" was a term used to denote precious stones and pigments of a particular blue, and Theophrastus mentions Egyptian *kyanos* as one of the three kinds available, the others being Scythian (possibly lapis lazuli) and Cyprian (possibly azurite). According to Theophrastus, the Egyptian *kyanos* was chosen for making pure pigments. In their interpretation of this comment, Caley and Richards maintained that Egyptian blue was used mostly pure, since any attempts to mix it with any other finely ground pigment would have been unsuccessful (Caley and Richards 1956: 55). Analysis of ancient paint layers has, however, shown this not to be the case: Egyptian blue has been identified in mixtures with white to create lighter tones, or mixed with red to form purple (Kakoulli 1999 and 2001).

Theophrastus also refers to the use of copper for the manufacture of glass, to provide a fine colour (after Davy 1815: 109). However, no other information is given for the production of Egyptian blue, the manufacture of which seems to have been regarded as one with other glasses and glazes.

In the Roman period, Pliny mentions two blue pigments, which he names *caeruleum*. The first, prepared by a wet process with the aid of plants and to be used on surfaces prepared with clay as the colour reacted with lime, is clearly some form of dye. The second, Vestorian, he mentions as costing 11 denarii per pound. He notes that this is made "from the finest part of Egyptian blue". He also mentions a Pozzuoli blue (or *cyanos*) — probably identical to

Vestorian blue — used to colour window glass (NH XXXIII, 158). Presumably this pigment was not affected by light.

In his book *De Architectura* (Vii, 11), Vitruvius also refers to a pigment with the name *caeruleum*; he says that although first produced in Alexandria, the pigment is also fabricated in Pozzuoli by Vestorius. Vitruvius provides a detailed account for its manufacture:

Methods of making blue were first discovered in Alexandria, and afterwards Vestorius set up the making of it at Puzzuoli. The method of obtaining it from the substances, of which it has been found to consist, is strange enough. Sand and the flowers of natron are brayed together so finely that the product is like meal, and copper is grated by means of coarse files over the mixture, like sawdust to form a conglomerate. Then it is made into balls by rolling it in the hands and thus bound together for drying. The dry balls are put in an earthen jar, and the jars in an oven. As soon as the copper and the sand grow hot and unite under the intensity of the fire, they mutually receive each other's sweat, relinquishing their peculiar qualities, and having lost their properties through the intensity of the fire, they are reduced to a blue colour.

Vitruvius does not refer at all to the use of calcium carbonate, one of the main constituents of the pigment. It is most likely that the sand used at Pozzuoli contained a high percentage of calcium carbonate. According to Ullrich (1987: 327), the Volturnus river (situated close to Pozzuoli) contains calcareous sand, and this may well have been the source of the raw material.

No other ancient documentary sources refer to Egyptian blue. For example, it is not mentioned in Egyptian papyrus, nor in any written sources (other than the tablet already referred to) from Mesopotamia and the rest of West Asia.

With the fall of the Romans, the technology of Egyptian blue was forgotten, and natural blue pigments such as azurite took its place. However, two much later occurences of Egyptian blue in the West are dated around the ninth century AD (Lazzarini 1982).

Modern studies and formulae

Many researchers with different interests have tried to reproduce the manufacture of Egyptian blue (Riederer 1997: 32). Some experiments have proved relatively successful, producing a material close to the ancient pigment. However, most studies have concentrated on the composition of the material alone, without taking into account its microstructure.

Studies concerning the technology of Egyptian blue started as early as the beginning of the 19th century. At first, Chaptal and Sir Humphrey Davy showed an interest in the blue pigment and published the first qualitative results. During the end of the first quarter of the 19th century, qualitative analyses of the pigment were published by Vauquelin (1826), Rammelsberg (1872) and De Fontenoy (1874), followed by Fouqué and Russell who published their results at the end of the 19th century. Analyses on Egyptian blue continued throughout the 20th century with data published by Crow in 1903 (Lucas and Harris 1962) and Le Chatelier (1907). Results on the same subject were also published by Eibner (1926), Granger (1933) and Lucas and Harris (1962). Chase (1971) also investigated the firing temperatures and firing atmospheres. Chase found the ideal temperature for the production of Egyptian blue to be 830–850°C in an oxidising atmosphere; higher temperatures fuse the mixture into a glass. Bayer and Wiedemann (1977) applied thermal differential analysis to understand the formation and stability of the pigment and Ullrich (1987) carried out a more systematic work, concentrating on the firing temperatures, times, alkali concentrations and grain size of raw materials.

Most recent works include Tite et al. (1984) with the study of ancient Egyptian blue samples from Egypt and Mesopotamia and Roman examples from the west of Europe and experimental trials for the reproduction of a wide range of fabrics, and El Goresy et al. (1986: 15–17) with the study of samples from the Old and New Kingdom. According to them Egyptian blue was manufactured in reducing conditions at temperatures not exceeding 740°C, so that pyrite was not decomposed under oxidising conditions; the mineral decomposes at 400°C to form Fe_2O_3 and SO_2. El Goresy et al. claim that the temperature used for the production of Egyptian blue during the Old Kingdom was higher than the temperature used during the New Kingdom, since during the latter period the pigment is very rich in glass. The presence of quartz in samples indicates that the mixture was not melted completely and regrinding and sintering of the mixtures was necessary to increase the proportion of blue crystals. El Goresy believes that during the New Kingdom Egyptian blue was made by quenching the silicate melt. The presence of titanomagnetite suggests that the sand used was of desert origin.

Cassiterite (SnO_2) can often be identified in Egyptian blue samples from the fifth Dynasty (the reign of Thutmosis III) up to the Roman period. Its presence is important, since it marks an innovation in the manufacture of Egyptian blue: the introduction of a new source of copper-bearing alloy, bronze.

Bronzes were probably imported, and according to El Goresy et al. (1986: 16) their use in the manufacture of Egyptian blue "may suggest the first recycling process known in ancient history". The use of bronze as the source for copper requires oxidising conditions, to allow the formation of an oxide, which can subsequently dissolve and crystallise as cuprorivaite. If reducing conditions were required for the manufacture of Egyptian blue when copper sulphide ores were used, to introduce bronze a preliminary oxidation of the copper would be required. It is therefore possible that an intermediate firing of the copper, in an oxidising atmosphere, took place prior to the introduction of SiO_2, CaO and the fluxes. Recent research by Pradell et al. (2006) has shown that the Egyptian blue crystals are formed through nucleation and growth within a liquid or glass melt even for mixtures with an alkali content as low as 0.3 wt%.

Analysis of ancient Egyptian blue pellets

Selected samples of Egyptian blue pigment pellets primarily from the Hellenistic period were analysed by means of polarised light microscopy (PLM), x-ray diffraction (XRD), micro-x-ray fluorescence (micro-XRF), environmental scanning electron microscopy (E-SEM), and scanning electron microscopy with energy dispersive spectroscopy and wavelength dispersive spectroscopy (SEM-EDS-WDS). The form of the pellets — essentially spherical, each about one centimetre in diameter — indicates that they are not secondary materials or by-products associated with the production of glass or faience, but deliberately made to be used as pigments.

The results from these analyses suggested at least three distinct classes of composition and two different microstructures. The most common composition of Egyptian blue contained crystals identical to cuprorivaite mineral, alkali glass (normally with fluxes of soda or potash), and residual quartz. The second type contains cuprorivaite crystals, leaded glass with low concentrations of alkalis and residual quartz. The last type of Egyptian blue contains only cyprorivaite crystals and residual quartz. There is no glass phase present. This composition might have resulted from successive firing and regrinding. Successive firing processes transform the glass phase into blue crystals, through sintering and quenching. Minor quantities of other elements present in the glass phase, such as iron, seem to derive from impurities in the sand used, while traces of tin and arsenic indicate the use of bronze as the source for copper.

The first type of microstructure identified was characterised by clusters of cuprorivaite crystals held together by interstitial glass particles and quartz. This was usually representative of the darker blue pellets having large particle sizes (Fig. 5). The second type had a much less ordered structure of only cuprorivaite crystals and quartz, organised in random orientations. The random orientation of particles — with no coherent matrix — in a pale blue sample from Delos (Fig. 6) suggests that the sample concerned was made from fine-grainned Egyptian blue and formed into pellets with water before being left to dry; there does not appear to have been a second firing in this case.

Experimental laboratory trials for the reproduction of Egyptian blue

Formulae and experimental manufacturing process

Based on data collected from the analysis of Egyptian blue pellets, scripts from primary literary sources and the results from previous technical studies, a series of experimental laboratory trials were formulated and implemented. The formulae and firing conditions chosen are summarised in Tables 1–3.

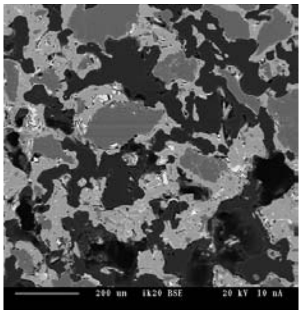
The raw materials, except for the bronze and copper, were sieved through 0.25 mm for coarse particles and 0.125 mm for fine particles. Bronze scraps were sieved through 0.5 mm, while copper scraps were finer, and were sieved through 0.25 mm.

Successive firings were carried out in order to evaluate the end product after each firing process. The resulting material after each firing was ground to a powder, sieved through 0.25 mm and 0.125 mm, and then remodelled into pellets using water or water with dissolved gum Arabic. The pellets were dried before re-firing.

Evaluation of the results of each firing was made with optical and instrumental analytical methods. Each method required special sample preparation, and care was taken, wherever possible, to ensure that the sample was retrievable and reusable for successive analysis.

The pigment pellets were cut in half to reveal the degree of reaction and fusion of materials, from the outer part to the core of the pellet. The resulting end products were examined with a binocular microscope, using oblique illumination provided by a fibre optic system, at magnifications between 6.3 and 40x. The examination of the unmounted samples under the binocular microscope was very important for the characterisation of the different phases present, and assisted the overall interpretation of the analytical results.

Polished sections were examined using a Leitz Orthoplan polarising microscope and an Omicron



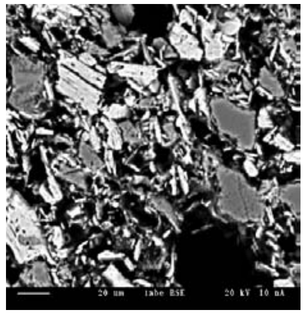


Figure 5 (left): Back scattered electron photomicrograph displaying the characteristic microstructure of dark blue Egyptian blue pigment. The image shows a coherent matrix of curporivaite with interstitial glass and residual quartz. [Photo: Kakoulli 1994]

Figure 6 (right): Back scattered electron photomicrograph displaying the characteristic microstructure of light blue Egyptian blue pigment. The image shows a random orientation of cuprorivaite and quartz particles suggesting regrinding and reshaping of the pellet. [Photo: Kakoulli 1994]

micro-XRF from Kevex Instruments. They were subsequently carbon-coated, for examination in the SEM. Qualitative analysis was carried out on a selected area of each section, or even on individual grains, using an EDS. Quantitative data were obtained using WDS.

Individual particles in powdered form were used for the preparation of other types of samples. Dispersions were made using Meltmount, with a refractive index of 1.662, and were examined primarily in transmitted light, both plane-polarised and under crossed polars.

Individual grains of the pigment were also mounted on double-sided carbon tape and examined using the E-SEM to image the microstructure.

Samples in powder form were analysed by XRD, using a Siemens 05005 x-ray diffractometer at 40 kV, 30 mA, and a 2 Theta range of 2–70 degrees. Time per step used was 0.4 s and the rotation speed 30 rpm.

Experimental results

Samples were examined with the aim of establishing the depth of reaction from the outer part of the pellets to the core, and the grouping of the various phases present in this multicomponent pigment. Observations using the binocular microscope combined with the XRD results are presented in a tabular form in Table 4 and in Figure 7.

The results varied according to the different formulae and firing conditions used. However, the main crystal phases detected were quartz and cuprorivaite, and — to a lesser extent — wollastonite and tenorite. Lead sulphate was detected in a single sample.

The microstructure varied slightly; most of the samples showed a coherent matrix of cuprorivaite crystals, interstitial amorphous glass and residual quartz, although the ratios and particle size varied.

Discussion and conclusion

The types of raw materials used and their preparation (particularly their granulometry) had an influence on the final products after firing. Significant differences in the nature of the pigment arise from differences in the source of copper (malachite, metallic copper, or bronze) and of sand. The experiments undertaken indicated that, for optimal production of Egyptian blue, rich siliceous sand ground to a fine powder is indispensable: the ideal particle size was found to be between 0.25 and 0.125 mm. The amounts and types of flux are also of importance.

Firing conditions also played a significant role: the temperatures, the length of time maximum temperature was maintained, and the number of firings influenced both the composition and the microstructure of the pigment. For the formulae tested in these experiments, with particle sizes between 0.25 and 0.125 mm, the firing temperature necessary for a good reaction was found to lie between 850°C and 950°C, for a minimum of 6 hours (Tables 1–3). Below and above this range of temperatures, the crystal phase of Egyptian blue could not form.

Tests of the effect of successive firing on the nature of Egyptian blue showed that secondary sintering produced deeper blues, whatever the granulometry of the reground material as more cuprorivaite crystals are formed. The light blue colour and the characteristic microstructure with particles in random orientation observed in one of the ancient pigment pellets might therefore suggest an air dried pigment pellet following the grinding of the pigment and its reshaping into a pellet.

Interpretation of the results, however, remains convoluted by the diversity of raw materials used during the manufacture of Egyptian blue, especially the source of copper and sand that influence the hues, composition and microstructure of the end product.

The diversity of Egyptian blue produced with changes in the ratios of raw materials therefore masks any patterns that could be indicative of provenance or trade of this pigment in the ancient world.

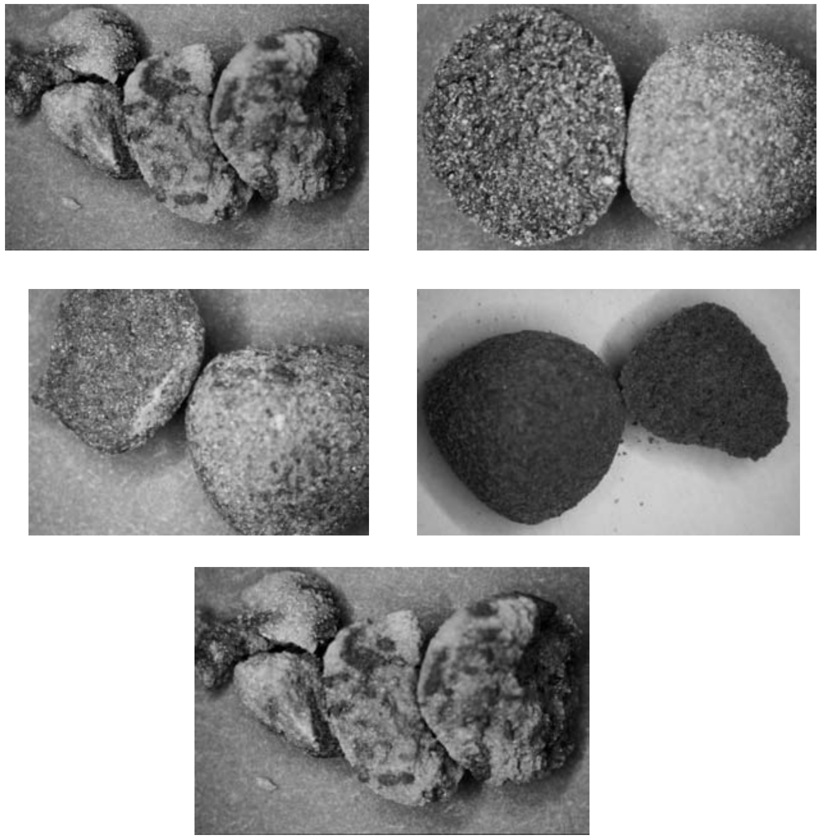


Figure 7: Photomicrographs at 6.3x magnification of experimental Egyptian blue pellets: Formula 1A – (a) after firing conditions III (top left), (b) after firing conditions IV (top right); Formula IC – (c) after firing condition III (middle left), (d) after double firing conditions V and VII (middle right); (e) Formula 4A after firing condition IV (bottom). [Photos: Kakoulli 1999]

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Note

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Table 1

Firing	Firing Conditions	‡ Formula 1A	‡ Formula 1B	Formula 1C	‡ Formula 2A	‡ Formula 2B
	• Atmosphere • Maximum temperature • Average change in temperature per minute • Time held at maximum temperature • cooling rate	64.6 g silica sand 7.2 g synthetic natron*** 15.4 g $Cu_2CO_3(OH)_2$ 12.8 g $CaCO_3$ * The particle size of the mixture is 0.25>mixture>0.125 mm	64.6 g silica sand 7.2 g synthetic natron 15.4 g $Cu_2CO_3(OH)_2$ 12.8 g $CaCO_3$ ** The particle size of the mixture is 0.125 >mixture	64.6 g silica sand 7.2 g synthetic natron 15.4 g $Cu_2CO_3(OH)_2$ 12.8 g $CaCO_3$ 0.87 g $PbCO_3$ Same composition and particle size (0.25>mixture>0.125 mm) as 1A with the addition of 1g of $PbCO_3$	64.6 g sand (Spectrum) (washed and ignited) 7.2 g synthetic natron 15.4 g $Cu_2CO_3(OH)_2$ 12.8 g $CaCO_3$ coarse sand >0.5mm	64.6 g sand (Spectrum) (washed and ignited) 7.2 g synthetic natron 15.4 g $Cu_2CO_3(OH)_2$ 12.8 g $CaCO_3$ coarse sand 0.5mm>x>0.25 mm
I	• covers over the crusibles • 830° C • Δ*t* 12° C /min • 60 minutes	na	na	na	Raw; For. 2A	Raw; For. 2B
II	• Oxidising • 900° C • Δ*t* 12° C /min • 20 hours	na	na	na	Raw; For. 2A Fir. I; For. 2A	Raw; For. 2B Fir. I; For. 2B
III	• Oxidising • 850° C • Δ*t* 12° C /min • 45 minutes	Raw; For. 1A	Raw; For. 1B	Raw; For. 1C	Fir. I; For. 2A (grind and re-shaped into a pellet)	Fir. I; For. 2A (grind and re-shaped into a pellet) Fir. I, II; For. 2B
IV	• Oxidising • 950° C • Δ*t* 12° C /min • 24 hour	Raw; For. IA	Raw; For 1B	na	na	na
V	• Oxidising • 950° C • Δ*t* 12° C /min • 6 hours •	Raw; For. 1A Fir. IV; For, 1A (regrind and sieved through 0.25 mm - labeled as 1Aa) Fir. IV; For. 1A (regrind and sieved through 0.125 mm – labeled as 1Ab) *Both 1Aa and 1Ab were re-shaped into a pellet using gum Arabic instead of water*	na	Raw; For.1C	na	na
VI	• Oxidising • 1100° C • Δ*t* 12° C /min • 6 hours	na	na	na	na	na
VII	• Oxidising • 850° C • Δ*t* 12° C /min • 6 hours	na	Fir. IV; For. 1B	Fir. III; For. 1C (regrind finely and pelleted using water) Fir. V; For. IC (regrind finely and re-shaped into a pellet using water)	na	na
VIII	• Oxidising • 850° C • Δ*t* 12° C /min • 24 hours	Raw; For. 1A	Raw; For. 1B	Raw; For. 1C	na	na

Table 2

FIRING	FIRING CONDITIONS	FORMULA 3A	FORMULA 3B	FORMULA 3C	FORMULA 3D	FORMULA 4A	FORMULA 4B
	• Atmosphere • Maximum temperature • Average change in temperature per minute • Time held at maximum temperature • cooling rate	62.31 g sand (Spectrum) (washed and ignited) 0.31 g K_2CO_3 1.77 g sodium sesquicarbonate 20.27 g $CaCO_3$ 6.09 g $PbCO_3$ 0.33 g SnO_2 1.98 g Fe_2O_3 23.71 g $Cu_2CO_3(OH)_2$ Sand sieved through 0.5 mm	62.31 g sand (Spectrum) (washed and ignited) 0.31 g K_2CO_3 1.77 g sodium sesquicarbonate 20.27 g $CaCO_3$ 6.09 g $PbCO_3$ 0.33 g SnO_2 1.98 g Fe_2O_3 23.71 g $Cu_2CO_3(OH)_2$ Sand sieved through 0.25 mm	62.31 g silica sand 0.31 g K_2CO_3 1.77 g sodium sesquicarbonate 20.27 g $CaCO_3$ 6.09 g $PbCO_3$ 0.33 g SnO_2 1.0 g Fe_2O_3 23.71 g $Cu_2CO_3(OH)_2$ * The particle size of the mixture is 0.25>mixture>0.125 mm	62.31 g silica sand 0.31 g K_2CO_3 1.77 g sodium sesquicarbonate 20.27 g $CaCO_3$ 6.09 g $PbCO_3$ 0.33 g SnO_2 23.71 g $Cu_2CO_3(OH)_2$ ** The particle size of the mixture is 0.125 >mixture	62.31 g silica sand 0.31 g K_2CO_3 1.77 g sodium sesquicarbonate 20.27 g $CaCO_3$ 16.91 g bronze 4.07 g $PbCO_3$ 1.0 g Fe_2O_3 (excess Sn: 1.32g) * The particle size of the mixture is 0.25>mixture>0.125 mm + added bronze	62.31 g silica sand 0.31 g K_2CO_3 1.77 g sodium sesquicarbonate 20.27 g $CaCO_3$ 16.91 g bronze 4.07 g $PbCO_3$ 1.0 g Fe_2O_3 (excess Sn: 1.32g) * The particle size of the mixture is 0.125 >mixture + added bronze
I	• covers over the crusibles • 830° C • Δt 12° C /min • 60 minutes	Raw; For. 3A	Raw; For. 3B	na	na	na	na
II	• Oxidising • 900° C • Δt 12° C /min • 20 hours	Raw; For. 3A Fir. I; For. 3A	Raw; For. 3B Fir. I; For. 3B	na	na	na	na
III	• Oxidising • 850° C • Δt 12° C /min • 40 hours	Fir. I; For. 3A (grind and re-shaped into a pellet)	Fir. I; For. 3B (grind and re-shaped into a pellet) Fir. I , II; For 3B	na	na	na	na
IV	• Oxidising • 950° C • Δt 12° C /min • 24 hours	na	na	Raw; For. 3C		Raw; For. 4A	na
V	• Oxidising • 950° C • Δt 12° C /min • 6 hours	na	na	Raw; For 3C	na	na	na
VI	• Oxidising • 1100° C • Δt 12° C /min • 6 hours	na	na	na	Raw: For. 3D	Fir. IV; For. 4A	Raw; For. 4B
VII	• Oxidising • 850° C • Δt 12° C /min • 6 hours	na	na	Fir. IV; For. 3C	na	na	na

Table 3

	temperature • Average change in temperature per minute • Time held at maximum temperature • cooling rate	1.77 g sodium sesqui 20.27 g $CaCO_3$ 6.09 g $PbCO_3$ 0.33 g SnO_2 1.0 g F_2O_3 13.63 g Cu * The particle size of the mixture is 0.25>mixture>0.125 mm + added bronze	8.85 g copper 12.8 g $CaCO_3$ 0.87 g $PbCO_3$ 0.33 g SnO_2 0.5 g Fe_2O_3 * The particle size of the mixture is 0.25>mixture>0.125 mm + added copper	15.4 g of malachite 12.8 g $CaCO_3$ 0.87 g $PbCO_3$ 0.33 g SnO_2 0.5 g Fe_2O_3 * The particle size of the mixture is 0.25>mixture>0.125 mm	15.4 g of malachite 12.8 g $CaCO_3$ 0.87 g $PbCO_3$ 0.33 g SnO_2 0.5 g Fe_2O_3 * The particle size of the mixture is 0.125 mm> mixture	12.8 g $CaCO_3$ 6.09 g $PbCO_3$ 0.31 g K_2CO_3 1.77 g sodium sesqui 0.33 g SnO_2 0.5 g $Fe2O_3$ * The particle size of the mixture is 0.25>mixture>0.125 mm	12.8 g C 6.09 g Pl 0.31 g K 1.77 g sc sesquicar 0.33 g Sı 0.5 g Fı * The par the mixtu 0.125 mm
V	• Oxidising • 950° C • Δt 12° C /min • 6 hours	Raw; For. 5	Raw; For.6	na	na	na	na
VI	• Oxidising • 1100° C • Δt 12° C /min • 6 hours	Raw; For. 5	Raw; For. 6	na	na	na	na
VII	• Oxidising • 850° C • Δt 12° C /min • 6 hours	na	na	na	Raw; For 7B	Raw; For 8A	Raw; For
VIII	• Oxidising • 850° C • Δt 12° C /min • 24 hours	na	na	Raw; For. 7A	Raw; For 7B	Raw; For 8A	Raw; For

‡ After Laurie [1914] and Chase [1971 (see formula II in Table 5.2)]. Different types of sand and particle size were tested.
* The mixture was ground to a fine powder. First the fusion mixture was ground together with the natron and malachite using acetone and then the silica sand was introduced. The mixture was ground together and sieved through 0.25 mm
** The mixture was ground to a fine powder. First the fusion mixture was ground together with the natron and malachite using acetone and then the silica sand was introduced. The mixture was ground together and sieved through 0.125 mm.
*** Trona or Synthetic
Natron [after Laurie *et al.*
1915, 426 and Chase 1971, 83]
32.6 g sodium
sesquicarbonate
20.8 g sodium sulphate
15 g sodium chloride

Table 4

Formula	Firing	Colour	Reaction	Reaction status	Results from XRD
1A	III	Greenish-blue	1	The fusion is very external. Only the first millimeter of the pellet has fused to glass with some blue crystals. The core changed into grey.	Quartz and wollastonite
1A	IV	Bluish-green	3	It seems that the material is fused completely. The pellet is blue throughout with dispersed green particles.	Cuprorivaite, a small quantity of wollastonite and residual quartz. A strong peak appeared at a d spacing of around 4.035.
1A	V	Bluish-green	2	Very similar in appearance to 1A, IV but there are some green particles on the exterior of the pellet. The core is primarily blue with a few dispersed green particles.	Cuprorivaite, a small quantity of wollastonite and residual quartz
1A	VIII	Bluish-green	1	Very external, and not complete reaction. Most particles turned green, rather than blue. Some reaction towards the core but not much. The core is dark grey.	Quartz and wollastonite
1Aa	IV and V	Dark blue	3	Complete reaction. It seems that most of the green particles (visible during the first firing 1A, IV) have disappeared and more crystalline blue is formed. Residual quartz can also be seen and probably very few dispersed green particles.	Cuprorivaite, a small quantity of wollastonite and residual quartz. A strong peak appeared at a d spacing of around 4.035.
1Ab	IV and V	Dark blue (same as previous)	3	Very similar in appearance to 1Aa. It is worth noting that although the particle size of this sample is smaller than 1Aa the colour obtained has the same intensity.	Cuprorivaite, a small quantity of wollastonite and residual quartz. A strong peak appeared at a d spacing of around 4.035.
1B	IV	Dark greyish-blue	4	The reaction seems to be homogeneous from the outer part to the core. The colour is mainly greyish blue throughout.	Cuprorivaite and residual quartz. A strong peak appeared at a d spacing of around 4.035.
1B	IV, VII	Dark blue (navy blue)	4	The pellet is dark blue with lots of black particles and residual quartz.	Cuprorivaite and quartz
1B	VIII	Whitish	6	External reaction turning whitish with green and blue inclusions.	?
1C	III	Blue	3	The whole pellet seems to have reacted, however, some green and grey particles are staining the exterior of the pellet. The pellet is quite compact.	Cuprorivaite and quartz
1C	V	Dark blue	3	The pellet shows a complete reaction, and has a dark blue colour, almost as deep as that of 1Aa and 1Ab. The core of the sample is darker than the outer shells. The exterior has also green particles.	Cuprorivaite and quartz
1C	III, VII	Deep blue (like ultramarine)	3	Almost all green particles have disappeared. A few black particles can only be seen, mainly on the exterior. The pellet is compact but not very hard. It has a moderate porosity similar to the ancient pellets.	Cuprorivaite and quartz
1C	V, VII	Deep blue (like ultramarine)	3	The whole pellet turned into blue. The pellet is not too hard and has a moderate porosity.	Cuprorivaite and quartz
1C	VIII	Blue	between 2-3	The pellet has almost a complete reaction with only the core appearing a bit green.	Cuprorivaite and quartz
3C	IV	Greenish-blue	4	Both the exterior and the core of the pellet have exactly the same colour (greenish blue). The pellet is very homogenous with distinct phases of blue, green black and transparent particles.	Cuprorivaite and quartz

Table 4: Continued.

Formula	Firing	Colour	Reaction	Reaction status	Results from XRD
3C	V	Greenish-blue	4	Very similar in appearance to 3C, IV.	Cuprorivaite and quartz
3C	IV, VII	Greenish-blue	4	Very similar in appearance to 3C, IV.	Cuprorivaite and quartz
4A	IV	Greenish-yellow	4	Mixture of light green, blue, whitish and solid bronze scarps throughout. However, the bronze scarps seem to have been altered with the firing. The reaction was homogenous from the exterior to the core, but not complete.	Unreacted bronze, cuprorivaite, quartz, tenorite and wollastonite
5	V	Greenish-yellow	2	Greenish yellow on the surface and grey in the core. Green, yellowish and black particles can be observed. The black particles are probably tenorite. It seems that the reaction was not complete. No blue crystals visible.	Tenorite
6	V	Dark green	5	Most of the copper fused and reacted with the other materials forming green particles. Black particles (probably altered copper) are also visible.	Unreacted copper, green amorphous particles, quartz and tenorite
7A	VII	Green	6	External reaction turning green. The interior altered to grey with blue inclusions.	Quartz, tenorite and wollastonite and amorphous green copper-baring glass
7A	VIII	Greenish-blue	2	The exterior of the pellet is green and blue, while the interior is more blue with almost no green particles visible. When the sample is studied in cross section, a ring can be observed towards the exterior which is altered into grey.	Cuprorivaite and quartz
7B	VII	Brownish (terracotta)	6	The exterior of the pellet has a terracotta colour crust while the interior is all grey-black.	Quartz, tenorite and lead oxide sulphate
7B	VIII	as above	as above	as above	Quartz, tenorite and lead oxide sulphate
8A	VII	Bluish-grey	4	The pellet has blue and black particles throughout. Homogeneous reaction from the exterior to the core.	Cuprorivaite and quartz
8A	VIII	Silvery blue	7	The pellet has a very light blue colour tinted particles however the core has more black particles that render the pellet darker towards the core.	Cuprorivaite and quartz
8B	VII	as 7A and 7B	as 7A and 7B	as 7A and 7B	Quartz and tenorite
8B	VIII	Black-blue		The pellet is hard and impossible to cut. The exterior shows black particles and few blue particles. The colour of the crust of the pellet has a unique colour and the particles seem to have spread homogeneously.	Quartz and tenorite

1. External reaction obtaining blue and green particles up to 2mm of thickness
2. Good and thorough reaction with blue and green crystals (more blue than green)
3. Complete reaction obtaining blue crystals. Only very few green particles
4. Homogeneous reaction from the exterior to the core, but not complete. Resulting to a mixture of blue, black and green
5. Homogeneous fusion and formation of deep green particles.
6. Poor reaction (general)
7. Moderate reaction (general)

Links between glazes and glass in mid-2nd millennium BC Mesopotamia and Egypt

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Abstract

This paper investigates the origins of glazing technology for clay-based ceramics. New analytical data are provided for glazes from 14th century BC Nuzi, Mesopotamia, which show that even the earliest glazes had similar compositions to contemporary glass. Slight compositional differences between glazes and glass are attributed to the influence of waste gases from the wood fuel used to fire pottery kilns. The results indicate that the technology for glazing ceramics in the Near East evolved from the glass industry. Technological reasons for the absence of glazed clay objects in Egypt prior to the 1st century BC are explored and discounted, and other explanations are proposed.

Introduction

Vitreous, glassy materials were intentionally made from an early date in the Near East and Egypt. Stones, such as quartz and steatite, were given glassy, coloured glazes and artefacts were also formed in faience, a material made from quartz particles sintered together and glazed with an alkali silicate glaze. In Mesopotamia, the earliest glazed faience, and potentially glazed steatite, $Mg_3[Si_8O_{20}](OH)_4$ (Deer et al. 1992), dates to the Ubaid period, 5400–4300 BC (Moorey 1994). In Egypt, glazed steatite and faience were produced during Predynastic times and Egyptian blue (a blue pigment containing crystals of copper calcium tetrasilicate, $CuCaSi_4O_{10}$, in a glassy matrix) was in use by the 3rd millennium BC. Glazed quartz was produced by at least the early third millennium BC and probably earlier.

There have been rare finds of glass beads and lumps of glass that date from 2100–2000 BC (Beck 1934; Moorey 1994). However, it is not until the middle of the second millennium BC that a range of glass objects, including core formed vessels and inlays, are found in considerable quantities across Mesopotamia and Egypt. Significantly, in Mesopotamia glazed clay objects were introduced at about the same time as widespread glass production. Amongst the earliest known glazed clay objects from the Near East are objects from Nuzi, now thought to date to the first half of the 14th century BC, and objects from Tell Atchana, levels VI-V, which are thought to precede the 15th century BC (Moorey 1989).

All of the ancient glassy materials described above, including the glazes on stones, faience and clay, and glass were based on the glass-forming compound silica (SiO_2), which has a melting temperature in excess of 1700°C. However, a reasonably low viscosity melt can be produced at around 1000°C if fluxes, such as the alkalis, soda (Na_2O) and potash (K_2O), or lead oxide (PbO), are added to the silica to lower the melting temperature. All of the Near Eastern and Egyptian glassy materials described above were produced using alkali fluxes. Possible sources of these fluxes include the ashes of plants, and mineral deposits, such as the evaporite natron, a form of hydrated sodium carbonate, found as efflorescence around soda lakes, for example at Wadi Natrun in Lower Egypt.

As both glass and glazes for clay objects appear to become widely used in the Near East at about the same time, and are similar alkali-fluxed materials, a potential link between the technologies for producing the two materials has been proposed. Attention has also been drawn to the fact that glazed clay-based

ceramics were not produced in Egypt until around the 1st century BC, although glass had been widely used in Egypt, as in Mesopotamia, from the mid-2nd millennium BC. Even then, the glazes eventually introduced in Egypt were lead-based and so compositionally very different from the alkali-based vitreous materials described previously. Subsequently, various technologically-based explanations as to why glazing clay was not possible in Egypt have been put forward. One such explanation is based on the fact that alkali-fluxed glazes are known to have high thermal expansion coefficients, and therefore shrink by large amounts as they cool down after firing. They are difficult to use with earthenware clays, which have much lower thermal expansion coefficients. A fault known as crazing generally results, in which a network of fine cracks forms in the glaze. It has been suggested that the alkali glazes used in antiquity were in this way physically incompatible with most earthenware clays and that this was overcome by some means in the Near East, but that in Egypt they lacked either the necessary raw materials or expertise (Hedges 1982; Vandiver 1982; Lucas and Harris 1962).

This paper is based on D.Phil. research on the development of vitreous materials in the ancient Near East and Egypt (Paynter 2001), supervised by Professor Mike Tite. The paper is in two parts, each addressing one of the following questions.

1. Is the technology for glazing clay-based ceramics linked to glass making in mid-2nd millennium BC Mesopotamia?
2. Why were glazed clay-based ceramics produced in Mesopotamia at this time, but not in Egypt?

A combination of literature information and artefact analysis was used to gather compositional data on alkali glasses, glazes and clays from Mesopotamia and Egypt. These data were compared to determine whether ancient glasses and glazes are compositionally linked and how these materials were produced. Experiments on replicate glaze compositions were also conducted, to investigate the compatibility of an alkali glaze with different substrates.

Analytical methods

Electron microscopy and a combination of EDS (energy dispersive spectrometry) and WDS (wavelength dispersive spectrometry) were used for the majority of this research. A Cameca SU30 WDS system with microprobe was used to obtain quantitative analyses of glazes and occasionally for phase analyses. Typically analyses were conducted at 4000 times magnification and the point size was approximately 25 microns x 30 microns. Higher magnifications were rarely used for soda glasses and glazes because this caused the sodium in the samples to volatilise. Operating conditions were a beam current of 10nA and an accelerating voltage of 20kV for WDS. An EDS spectrometer with Oxford Instruments Isis software was occasionally used quantitatively for heterogeneous materials, such as clay substrates, to analyse larger areas at lower magnifications. The detection limit for most elements with EDS was about 0.1%. The EDS results are normalised to 100% to allow comparison of the data, as the clays contained large regions of porosity and the analytical totals are correspondingly variable. With WDS the detection limits were an order of magnitude better and the data are given unnormalised. Analyses of standard reference materials confirmed the accuracy and precision of the results (Paynter 2001).

Glass

Literature data

Literature data on the composition of glass from Mesopotamia and Egypt are collated in the Tables 1 and 2. There are a number of variables that can result in large differences between reported glass compositions, which were considered when selecting data. For example different glass colours contain different colourants and so only the major elements have been listed in the tables, the colourants, opacifiers and decolourisers have been omitted, and the oxides normalised. Data on New Kingdom cobalt blue glass are omitted from Table 2 because this type of glass has a unique composition with low levels of potash but quite high levels of magnesia and alumina, as a result of the type of alkali flux and colourants used, both of which have been the subject of recent debate (Lilyquist and Brill 1993; Rehren 2001; Shortland 2000; Tite and Shortland 2003; Kaczmarczyk 1986). A range of analytical techniques were used to obtain these results, and this must be taken into account. Also, glassy materials are susceptible to damage by water, which can result in reduced levels of oxides such as sodium. Analyses, in particular those with less than 10wt% soda, were cross-referenced with a ternary phase diagram for calcium, sodium and silicon oxides, with a constant 5wt% magnesium oxide. This provided an indication as to whether a glass with the composition in question might be produced at feasible temperatures (Shahid and Glasser 1972; Rehren 2000). As a result, some analyses were

Table 1: Literature compositional data on Mesopotamian glasses

Date	Site	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	FeO	Source
2250 BC	Tell Brak	14.55	2.09	1.68	72.42	0.05	9.08	0.14	Brill 1999
~2100 BC	Eridu	17.34	3.47	2.55	66.31	4.59	3.57	2.17	Garner 1956
1300 BC	Tell Brak	16.77	3.10	0.25	69.46	1.72	8.61	0.09	Brill 1999
		15.64	4.32	0.88	65.62	2.06	11.14	0.33	
		14.88	2.69	0.40	73.34	1.69	6.90	0.10	
		16.32	5.55	0.39	67.23	3.09	7.34	0.07	
		13.75	5.37	0.30	69.52	2.33	8.66	0.07	
		16.36	5.40	1.01	65.24	3.90	7.61	0.48	
1450–1350 BC	Nuzi	17.16	5.00	0.84	65.43	2.44	8.85	0.28	
		15.05	4.03	0.43	68.50	3.19	8.60	0.19	
		18.31	4.87	1.42	65.43	2.41	6.66	0.91	
		15.85	4.70	0.43	71.25	2.33	5.23	0.21	
		17.21	4.87	0.95	65.56	2.94	8.03	0.44	
		12.16	3.96	0.42	74.76	2.04	6.46	0.21	
		13.08	5.47	1.05	70.47	3.57	6.08	0.28	
		15.50	3.61	0.51	67.30	2.50	9.69	0.89	
		13.58	3.20	0.43	70.06	2.43	9.70	0.61	
		17.47	4.94	0.72	65.41	3.80	7.39	0.25	
		16.43	4.62	0.84	69.82	2.98	4.92	0.39	
14th C BC	Nuzi	14.17	3.14	0.81	70.32	2.74	8.60	0.22	Vandiver 1982
		11.82	3.58	1.44	71.20	3.85	7.75	0.36	
		14.13	6.19	2.27	68.66	3.29	5.23	0.23	
1450–1200 BC	Tell Al-Rimah	12.85	4.55	1.49	73.26	2.27	4.47	1.11	Brill 1999
1400 BC	Nippur	18.24	2.65	2.24	68.28	1.76	5.93	0.90	Caley 1962
		14.68	5.87	1.60	67.61	2.49	6.50	1.26	

omitted. The artefacts analysed by Lilyquist and Brill originate from a variety of tombs and other locations, and so site information has not been given for each object, but all are from securely dated contexts or carry datable inscriptions.

The levels of potash and magnesia observed in the Mesopotamian and Egyptian glasses are indicative of a plant ash source of alkalis (Sayre and Smith 1961 and 1974). Relatively few of the glasses contain high levels of alumina and so a low-alumina silica source, such as quartz pebbles, may have been used rather than sand (Freestone and Gorin-Rosen 1999, 111; Rye and Evans 1976; Brill 1999). As plant ashes contain variable levels of lime, it would have been possible to produce glasses with this type of composition from quartz pebbles and plant ashes only, without needing to add lime, as demonstrated by Brill (1970) and discussed more recently by Freestone and Gorin-Rosen (1999). A relatively wide range of potash and magnesia contents is observed in the glasses and the differing ratio of potash to magnesia indicates that these are unlikely to simply be dilution effects. This variation may be due in part to the natural diversity of plant ashes between different species, different plants or parts of plants within the same species, and varying seasons and areas. Other factors likely to contribute are processing and production variables and the analytical methods used to obtain the data.

The archaeological record indicates that plant ash type glasses were worked in New Kingdom Egypt and crucibles for glass production have been found (Rehren 1997). Nevertheless the great compositional similarity of most Mesopotamian and Egyptian glasses has led to speculation as to whether Egyptian artisans possessed the ability to make glass in the early stages of this technology, or whether glass cullet was imported from elsewhere to supply glass workshops. However other explanations for this similarity have been put forward. A fairly small compositional window exists for a chemically stable, transparent glass with a viscosity suitable for melting and working at the temperatures of around 1100°C attainable in antiquity. Rehren (2000) points out that the composition of the final glass would have been influenced by the temperature at which the raw materials were heated, as well as the overall composition of the raw materials batch, since the raw materials may not have dissolved in entirety.

Table 2: Literature compositional data on Egyptian glasses (excl. cobalt-coloured)

Date	Site	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	FeO	Source
1348–1335 BC	Amarna	16.39	3.62	1.33	69.29	1.34	7.44	0.60	Brill 1999
		17.32	3.97	0.58	65.99	2.57	9.26	0.30	
		23.31	4.73	1.11	58.27	1.25	10.77	0.56	
		20.81	3.34	1.02	64.54	1.73	8.01	0.55	
		19.22	4.52	0.53	62.27	2.64	10.13	0.67	
		18.32	4.10	0.76	65.81	1.72	8.87	0.41	
		18.93	3.62	0.65	65.92	2.96	7.46	0.46	
		18.25	4.06	0.90	67.12	2.15	6.59	0.94	
		17.99	4.12	0.65	65.58	2.88	7.82	0.97	
		18.71	2.83	1.06	68.33	1.13	6.62	1.32	
		17.15	3.28	1.23	68.37	1.63	7.21	1.12	
		18.53	3.36	0.42	67.51	2.60	7.36	0.22	
1479–1401 BC	Various	20.8	5.7	1.7	65.4	2.2	4.0	0.3	Lilyquist and Brill 1993
1479–1425 BC	Various	17.9	6.2	1.3	63.5	3.1	7.5	0.5	
		18.0	5.04	0.8	66.6	3.1	6.0	0.5	
		18.5	2.8	2.9	62.0	2.6	7.8	3.1	
		18.8	2.8	0.8	70.1	3.8	3.3	0.5	
		19.6	3.9	0.6	66.9	3.6	5.0	0.4	
1479–1425 BC	Various	15.8	5.8	1.2	63.5	4.3	9.0	0.4	
		16.7	3.8	0.8	65.5	3.5	9.2	0.4	
1427–1401 BC	Various	18.4	5.3	0.9	64.6	2.3	8.0	0.4	Lilyquist and Brill 1993
		19.9	5.2	0.6	64.8	2.6	6.7	0.3	
		20.5	4.4	0.6	64.2	1.9	8.1	0.4	
		18.4	3.7	0.6	64.7	2.4	9.9	0.3	
		17.5	4.6	0.7	64.3	2.9	9.6	0.4	
		19.7	5.2	0.7	64.3	2.4	7.4	0.3	
		19.0	4.7	0.7	65.1	2.9	7.4	0.3	
		20.3	4.7	2.5	63.5	2.7	7.1	0.4	
		10.8	5.4	0.9	63.2	2.4	6.8	0.5	
		17.8	4.3	1.7	63.2	2.6	9.9	0.5	
		19.3	5.0	0.5	65.1	2.3	7.5	0.3	
		18.8	4.8	0.5	65.3	2.9	7.4	0.4	
		20.2	5.6	0.8	64.1	1.8	7.0	0.4	
		16.5	3.8	1.3	64.7	2.7	10.4	0.6	
		19.3	4.8	0.6	65.6	2.4	7.0	0.3	
		10.4	5.0	0.7	64.8	2.2	6.5	0.4	
1401–1391 BC	Various	19.0	5.3	1.3	64.4	2.8	6.6	0.5	
		20.8	4.3	1.0	62.1	2.6	8.8	0.4	
		19.8	4.4	0.9	65.2	2.0	7.4	0.4	
~1540–1070 BC	Qantir	18.04	4.85	1.58	64.49	1.80	8.79	0.45	Rehren 1997
		18.16	3.48	0.84	66.42	2.01	8.76	0.32	
		20.56	4.91	0.73	63.57	1.98	7.93	0.31	

Glazes

Literature Data

In Table 3, compositional data from literature sources are compiled for glazes on clay objects, using only the major constituents normalised to 100%.

Analyses of glazed clay artefacts

Samples of four glazed clay artefacts from Nuzi, Mesopotamia, probably dating to the 14th century BC, were generously provided by the Peabody Museum, Boston and were examined using scanning electron microscopy. Weathered areas of glazes

appeared dark grey in the back-scattered electron SEM images and unweathered areas were light grey (Figs. 1, 3 and 4). Only unweathered regions of glaze were selected for WDS analysis. Where sufficient clay sample was present, the clay was analysed by EDS. Two samples of glaze were examined from vessel 1930.16.3 and also from wall nail 1931.1.162, plus a single sample from wall nail 1930.2.271. The preservation of the glaze sample from vessel 1930.16.1 was too poor for any data on either the glaze or clay to be obtained.

The composition of the clay associated with samples 1930.16.3 and 1931.1.162 was determined using EDS analysis (Table 4) and is consistent with literature data (given in Paynter 2001: 78) for Mesopotamian alluvial clays. The clay was calcareous but also contained significant concentrations of magnesia.

The glazes were all about 1mm thick. The glaze on sample 1930.16.3 was very well preserved and homogeneous, containing little undissolved or crystalline material. However the glaze contained many small bubbles, the majority less than 4mm in diameter (Figs. 1 and 2). This glaze sample was the only one well enough preserved for analyses of the glaze bulk to be obtained (Table 5, bulk composition on first row, see appendix Table 7 for full data). The glaze was alkali-fluxed and the presence of significant quantities of both magnesia and potash suggests that plant ashes were the source of the alkalis. The glaze contains little iron oxide or alumina and the concentration of potash is higher than the concentration of magnesia.

The glazes on the remaining samples were completely weathered with the exception of interaction regions that had formed during firing at the interface between glaze and clay (Fig. 3). The interaction zones were between 40 and 50 microns thick in total and had characteristic microstructures, which were formed when some of the clay from the substrate dissolved in the adjacent glaze. This resulted in a region of glaze becoming enriched in lime, alumina, magnesia and iron oxide, all of which are present in

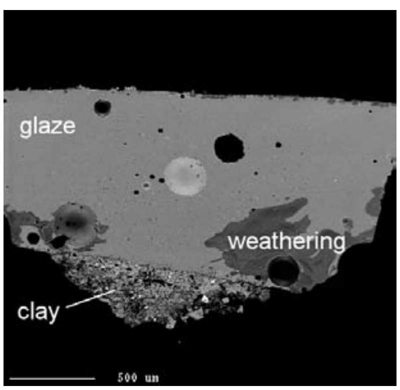


Figure 1: Back-scattered electron image of well preserved glaze with clay substrate from Nuzi artefact 1930.16.3.

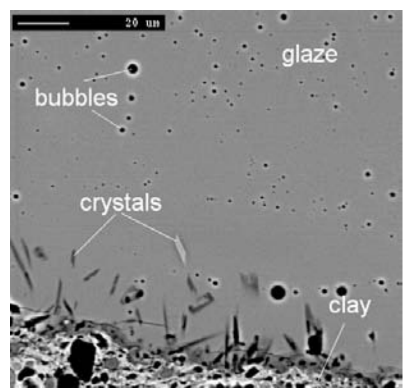


Figure 2: Back-scattered electron image of interaction zone between glaze and clay from Nuzi artefact 1930.16.3.

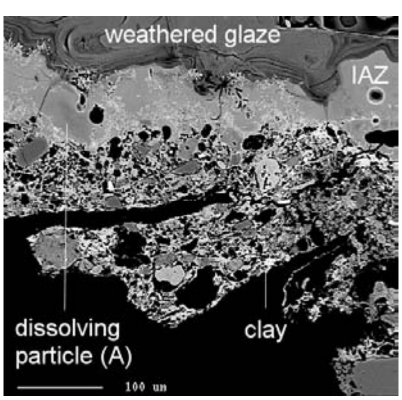


Figure 3: Back-scattered electron image of interaction zone between clay and glaze on Nuzi artefact 1931.1.162.

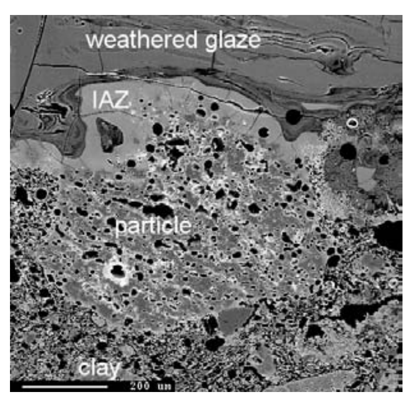


Figure 4: Back-scattered electron image of partially dissolved argillaceous particle at the interface between glaze and clay on Nuzi artefact 1931.1.162.

quite large quantities in the clay. The high, localised concentrations of lime, magnesia and iron oxide caused crystals to form at the interface. Therefore the interaction zones generally consisted of various layers, the first being made up of glaze-saturated clay (Fig. 3) containing some small crystals (light or dark grey, angular forms and occasionally black holes if the crystals had been pulled-out). Clusters of larger crystals were often present above this region, further into the glaze. The crystals were identified as pyroxenes, such as augite and diopside. The interaction zones also contained occasional patches of crystal-free, alumina-rich glaze.

In the well-preserved sample from object 1930.16.3 very little interaction is observed between the glaze and clay (Fig. 2), with only occasional crystals at the interface. This suggests that this object may have been fired at a slightly lower temperature or for less time than the other objects. This is consistent with the small bubbles observed in the glaze of sample 1930.16.3. The results of experiments comparing the homogeneity of unfritted versus fritted glazes for a range of firing regimes (Paynter 2001) suggest that the raw materials for this thick, homogeneous glaze were probably fritted before being applied.

In the samples from objects 1931.1.162 and 1930.2.271 there was greater interaction between glaze and clay but the only surviving areas of un-weathered glaze were within these interaction zones. 15 areas could be analysed by WDS in the former sample but only two areas in the latter sample (Table 5, average interaction zone (IAZ) compositions in second and third rows). The full data are available in the appendix, Table 8. The compositions of the glazes within the interaction zones are similar to the data previously reported for samples from a Nuzi artefact (Vandiver 1982), also given in Table 5 (final row), with abnormally high alumina contents and elevated levels of iron oxide relative to typical analyses of plant ash glazes (Table 3). In contrast the lime and magnesia concentrations are lower than typical. It is unlikely that these compositions are representative of the glaze as a whole. Experiments replicating Mesopotamian glazes on various types of clay substrate (Paynter 2001) have shown that the composition of the glaze in the interaction zone differs from that of the glaze bulk. It is likely that this difference in composition is responsible for the preferential survival of these areas of glaze as the increased alumina content in that region increases weathering resistance. Also pyroxene crystals were often present within the glaze interaction zone but absent in the areas that were particularly alumina-rich (Swift 1947), and so these crystal-free, alumina-rich areas tended to be selected for analysis.

In the artefacts examined the regions of crystal-free glaze within the interaction zones were generally localised, rather than spread uniformly along the clay / glaze interface. In some areas the faint outlines of dissolving alumina-rich mineral grains were still discernible (darker grey region (A) indicated in figure 3) and in others, the remains of large, fine-grained, vesicular, argillaceous particles were often situated within, or adjacent to, un-weathered areas of interaction zone glaze, as shown in Figure 4. These particles had partially vitrified during firing and, when located at the clay / glaze interface, had dissolved more rapidly than surrounding minerals. Several of these mineral grains were observed in the clay substrates of the samples and they appeared to be natural components of the clay. They had varying compositions, containing mixtures of quartz, alkali feldspars and fine micaceous minerals, but analysis showed that they were generally rich in alkalis, predominantly potash (~5 wt%) and some soda (~3 wt%), iron oxide (~9 wt%), alumina (~13 wt%) and silica (~68 wt%).

Given that only analyses of un-weathered areas within the bulk of the glaze can be considered representative of the glaze composition, the Nuzi data indicate that early glazes probably had compositions comparable to glazes of later date (Table 5). In none of these samples was any evidence found to suggest that slips or clay temper might have been deliberately added to increase the thermal expansion coefficient of the clay body in order to improve the compatibility of clay and glaze and thereby reduce the severity of crazing.

Are the technologies for glass making and glazing clay-based ceramics linked?

Differences between glass and glaze compositions

The compositions of the Mesopotamian alkali glasses and alkali glazes applied to clay objects (Tables 1 and 3) are very similar but there are slight differences. The alkali glazes often contain slightly more potash, alumina and iron oxide than the glasses and the soda contents are towards the higher end of the range observed for glasses. Whilst the alumina, iron oxide and soda contents of the glazes are variable, the amount of potash exceeds the amount of magnesia in the glazes fairly consistently, whereas the opposite is true of most glasses. This is illustrated in Figure 5, where potash has been plotted versus magnesia for glasses and glazes of the Near East and Egypt prior to the 1st century BC, using the data in Tables 1, 2, 3 and the first row of Table 5. The glasses and glazes largely group separately, with the notable exception being the Eridu glass sample. Literature data for other

Table 3: Literature compositional data on Mesopotamian glazes.

Date	Source	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	FeO	Source
13th c. BC	Tell Brak	17.0	0.7	2.6	70.4	0.9	8.1	0.4	Oates et al. 1998
580 BC	Babylon	18.0	3.7	1.9	64.6	4.3	6.0	1.4	Matson 1986
		18.1	3.4	0.8	67.3	4.4	4.9	1.0	
		20.0	4.0	2.0	62.7	3.9	6.1	1.1	
		18.9	3.7	1.5	64.1	4.1	6.4	1.3	
		16.3	4.5	1.5	65.9	4.6	6.3	0.9	
		15.0	3.9	2.1	66.9	3.9	6.9	1.2	
		17.5	4.2	2.1	63.3	3.7	7.9	1.2	
		16.9	4.3	1.4	65.1	4.2	5.9	2.0	
		17.1	4.2	2.2	63.6	4.1	6.6	2.0	
		16.9	4.1	2.2	64.3	3.7	7.2	1.5	
580 BC	Babylon	18.2	4.6	1.0	64.7	4.6	5.9	0.9	
Seleucid	Nippur	11.1	4.0	3.0	63.3	5.0	7.8	5.4	McCarthy 1996
		12.6	3.9	1.5	62.5	5.2	6.6	6.9	
3rd c. BC	Nippur	12.7	2.7	2.3	63.4	5.2	7.5	5.7	Tite and Mason 1997
~175 BC to 150 BC		19.6	2.4	2.8	62.0	4.5	7.3	1.3	
9th c. BC	Nimrud	10.3	2.0	3.6	72.9	5.1	5.1	1.1	Freestone 1991

Table 4: Clay composition, measured by EDS, normalised.

Sample	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	FeO
1930.16.3 (average 2 analyses)	1.4	4.1	9.2	58.2	0.8	21.3	0.6	0.1	4.2
1931.1.162 (single analysis)	2.1	3.7	11.3	63.1	2.3	10.8	0.7	0.2	5.7

Table 5: Composition of Nuzi glaze sample, compared to analysis of Nuzi glaze from Vandiver 1982

Sample	Area	Na_2O	MgO	Al_2O_3	SiO_2	PbO	K_2O	SnO_2	Sb_2O_3	CaO	TiO_2	MnO	FeO	CoO	CuO	Total
1930.16.3 (9)	Bulk	12.96	3.85	0.65	66.50	0.05	5.64	0.06	0.10	6.37	0.04	0.03	0.38	0.02	2.39	99.06
1931.1.162 (15)	IAZ	12.63	2.28	7.76	64.57	0.03	4.31	0.01	0.05	3.09	0.25	0.01	2.99	0.02	0.87	98.9
1930.2.271 (2)	IAZ	9.42	2.46	7.58	70.10	0.04	1.56	0.04	bd	2.75	0.30	0.01	2.47	bd	1.38	98.1
		1.06	1.52	18.01	69.02	0.06	1.77	bd	0.10	1.23	0.12	0.03	1.98	bd	1.01	95.9
Vandiver 1982		12.37	4.23	10.10	51.46	0.15	3.31	bd	nm	8.93	0.80	0.01	3.85	nm	1.37	96.6

periods and locations reveal a similar pattern (Paynter 2001). There is also some grouping of material from the same locations. This is to be expected due to factors such as raw material variability between regions and that material from separate sites was analysed in different studies.

The properties of a Mesopotamian glass and a glaze with typical compositions have been estimated using literature data on the properties of experimental glasses with similar compositions to the ancient materials (Mazurin et al. 1983 and 1987). These data indicate that both materials have similar maturing temperatures but that the glass composition might have a slightly lower thermal expansion coefficient because it contains less potash and more magnesia. The minor differences between glaze and glass do not appear to offer any significant advantages for the respective applications. If anything, the higher magnesia content found in the glass would offer benefits in glazing (see below). Therefore the compositional differences observed are likely to have been unintentional.

Sampling for analysis

Examination of glazed artefacts has demonstrated that regions of glaze within the interaction zone, at the glaze / clay interface, are less likely to be weathered than the bulk of the glaze, and are therefore more likely to be selected for analysis. However these areas of glaze are not representative of the glaze as a whole, being enriched in alumina and iron oxide. This might result in non-representative, high levels of alumina and iron oxide being reported for glazes relative to glasses.

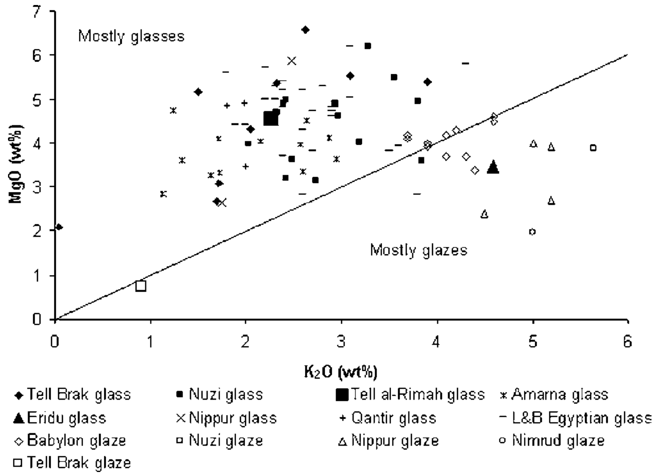


Figure 5: Potash versus magnesia for glasses and glazes from the Near East and Egypt, using data from Tables 1, 2, 3, and 5. The line represents a magnesia to potash ratio of 1; the majority of the glasses plot above this line and the majority of the glazes below it.

Addition of clay

The increase in alumina and iron oxide observed in some ancient glazes could be a result of clay entering the glaze, either unintentionally with other raw materials (see the section on raw materials selection), or added deliberately, for example to inhibit deflocculation (when the glaze settles out) if the glaze was applied from a suspension in water. However, a straightforward addition of Mesopotamian alluvial clay (Table 4) to a quantity of plant ash glass (Table 1) would not produce the correct composition for an ancient glaze (Table 3). Also some glazes, such as the Nuzi glaze analysed in this study, contain very little alumina or iron oxide although they still contain more potash than magnesia, and so the consistently higher potash contents of glazes relative to glasses cannot be explained in this way.

Diffusion from the clay

For the dissolution of lime-rich Mesopotamian clay in a glass to produce a composition typical of a glaze, alumina would be required to dissolve preferentially to the lime, but the opposite has been observed in experimental work (Paynter 2001). Even if this were not the case, because the interaction zones on the artefacts examined were in the order of 40 microns thick, insufficient clay would have dissolved during firing to bring the glazes, which were 1mm thick and largely homogenous, to the correct composition across the entire glaze thickness.

Raw materials selection

The source of silica used in glaze production would have influenced the amount of potash, alumina and iron oxide in the material. Quartz pebbles are thought to have been used for Mesopotamian glass production and analysis has shown that these are quite pure sources of silica (Brill 1970). In contrast sand can contain varying and often significant quantities of lime, potash, iron oxide and alumina (Brill 1999: 474–479), and when sand is used in glass production it influences the composition of the glass in diagnostic ways, as shown by Freestone et al. (2000). However it is unlikely that sand would contribute sufficient potash to account for the differences observed between glasses and glazes.

Another alternative is that plant ashes containing greater proportions of potash than magnesia (Brill 1970) may have been selected for glaze production whilst another type was used for glass production. As no technical advantage would be gained through this, the choice might reflect views on the quality, and appropriate applications, of different types of raw material at that time. Ethnographic studies in Pakistan have shown how the best plant ashes for producing vitreous materials are selected on the basis of their colour, smell and porosity (Rye and Evans 1976) and the fusibility of these ashes varies greatly. The demands of other industries, such as glass making, might also have influenced the availability and price of the raw materials available for glaze production. The composition of plant ashes is greatly influenced by the geology of the region where the plant grows (Sanderson and Hunter 1981). Workshops in different locations may have used ash from different sources, and so the composition of the ash would vary (Freestone pers. comm.).

Processing and production

Differences between the fritting, firing and refining stages used in the production of Mesopotamian glasses and glazes might result in compositional differences between these glassy materials, even if the compositions of the starting batches were the same (Rehren 2000). In an ethnographic study of pottery production in Pakistan, Rye and Evans (1976) describe the preferred use of hard-wood fuel in the kilns and several fritting stages during the preparation of glazes by potters, the first heating small balls of powdered glaze mixture in the firebox of the kiln amongst the fuel ashes. The final explanation considered for the differences between Mesopotamian glazes and glasses is that the materials may have had very similar compositions initially, but that the glaze composition was slightly altered during firing and /

or glaze preparation by the incorporation of potassium compounds from the fuel ash or more probably vapour. Glazes on pottery have a high ratio of surface area to volume and would be more likely to be compositionally affected by fuel ash or vapour relative to glass being heated in a crucible. Fuel ash would also be more likely to adhere to a surface covered with molten glaze than to an unglazed ceramic surface, although the effect would be anticipated to be non-uniform.

Potassium and sulphur are known to play a key role in the formation of deposits when certain wood fuels are used, as potassium and sulphur compounds volatilise at temperatures above 900°C (Misra et al. 1993). Many wood ashes contain potassium compounds as a major component (Sanderson and Hunter 1981; Turner 1956), although the proportions of different compounds present varies greatly with many factors, mentioned previously, including plant species and origins and firing temperature. No data on the composition of ash from hard wood species from the Near East were available. Data are only available for species with soda-rich ashes, such as the bushes growing in coastal and desert areas described by Ashtor and Cevidalli (1983: 496), and again there is great variation in composition. However fuel ashes have been proposed as the cause of the increased potash, and to a lesser extent, soda in glass making crucibles from New Kingdom Egypt (Rehren, 1997). Therefore this is probably the explanation for the increased levels of potash in glazes relative to glasses.

Summary

The glazes on Egyptian and Near Eastern steatite, quartz, faience and clay from different periods cannot be directly compared with one another as literature data show that the glazes have different compositions, microstructures and properties and thus were glazed in different ways. The earliest materials to be glazed with alkali glazes: quartz, faience and fired steatite, all contained ~65 wt% or more of silica. Investigation of the glazing methods used to produce these artefacts (Barthelemy de Saizieu and Bouquillon 1997; Bouqillon et al. 1995; Kaczmarczyk and Heges 1983; Paynter 2001; Shortland 2000; Shortland and Tite 1998; Tite and Bimson 1989; Vandiver 1998; Wulff 1966; Wulff et al. 1968) suggests that in many instances the silica content of the substrate was important to the chemistry of the glazing process and therefore the type of glazing methods that were successful. Together with other attributes of the materials, such as the abundance, ease of shaping and robustness during and after firing, and the cultural preferences of the artisans producing the objects, this dictated which materials were first glazed. As the types of clay glazed in the Near East from the mid-2nd millennium BC contained less silica than faience, quartz or fired steatite, glazing clay objects required a different approach.

A relationship between the technologies for glass making and glazing clay objects is very likely given that glazed clay objects and glass vessels appear in the archaeological record simultaneously. Peltenberg (1987) also described the typological similarity of glass vessels and glazed clay vessels from this period. Clay vessels were glazed on the outside, to obtain a glass-like lustrous, coloured surface, rather than the inside, to reduce the permeability of the vessel. Glazed clay objects were originally prestigious items, many intended for high status functions such as the decoration of temples. Glass making processes, and the appearance and demand for glass vessels themselves, are likely to have inspired the production of, and led to demand for, glazed clay objects.

In this study the closeness of the technological link between glass and glazes has been further explored by comparing the compositions of the two materials. Ancient alkali glazes and glasses are very similar, but small differences were identified. Some of these inconsistent differences may be due to factors such as raw material variation, and whether the areas of glaze selected for analysis are representative of the whole. However increased levels of potash relative to magnesia are consistently observed in glazes relative to glasses. A variety of reasons for this have been considered, including the selection of different types, qualities or sources, of raw materials by potters relative to glass workers and / or differences in the procedures for selecting, ashing, refining or fritting these materials. Other influences, such as diffusion of compounds from the clay, have been discounted. It is most likely that glazes and glass were produced from the same raw materials, and were compositionally similar, but that the glazes were then enriched in potash by exposure to waste gases, and to a lesser extent ash, from the wood fuel used to fire the pottery kilns.

Therefore this research supports the hypothesis that the technologies for making glass and glazing clay were closely related and used similar raw materials and processes. However the scale and distribution of production sites, and the methods used for obtaining and processing raw materials etc., may have differed considerably between the glass making and glazing crafts, not least because glaze production was an additional skill in a pre-existing industry: that of producing fired clay objects.

Why were glazed clay-based ceramics produced in mid-2nd millennium BC Mesopotamia, but not in Egypt?

Factors influencing alkali glaze compatibility with clays

Once a glaze has solidified on the surface of an object, it is constrained to shrink by the same amount as the object as cooling continues. It is better that the substrate contracts slightly more than the glaze, compressing it, as glazes are strong in compression but weak in tension. However most earthenware clays have lower thermal expansion coefficients than alkali-fluxed glazes. Therefore as an alkali-glazed clay object cools, the glaze stretches and eventually a fine network of cracks forms, known as crazing (Hamer and Hamer 1997). Crazing can be reduced by manipulation of the body, glaze and processing conditions. The main factors influencing crazing are discussed below (Kingery et al. 1976). Delayed crazing can also be observed in fired and glazed ceramics, when the ceramic absorbs water and expands. The glaze is stretched until eventually it cracks. This occurs with many archaeological artefacts during burial but in this study the emphasis is on original, rather than delayed, crazing.

Glaze properties

The difference between the thermal expansion coefficient of a glaze and the substrate to which it is applied is one of the most important factors influencing crazing, particularly over the temperature range ~500°C to ~25°C for the glaze compositions considered here (as the glaze is then solid and attached to the substrate, so both glaze and substrate must shrink by the same amount as they cool to room temperature). The thermal expansion coefficient of a glaze is dependent upon its composition. There are several published models for predicting the thermal expansion coefficients of glazes from their compositions, but they do not take interactions between different glaze components into account and so may be accurate to no more than a degree of magnitude. However these models provide a useful indicator of the relative influence of each oxide on glaze thermal expansion coefficients. For example soda increases the thermal expansion coefficient by the greatest amount, followed by potash, lime, lead oxide, magnesia and alumina.

Lists of the properties of glassy materials with different compositions are also available in the literature and have been used in this study to predict glaze and glass properties (Bansal and Doremus 1986; Mazurin et al. 1983 and 1987) in preference to the models described previously. Some typical thermal expansion coefficients of earthenware glazes, both lead- and alkali-fluxed, are given in Table 6. Although not all of the references state the temperature range or type (volume or linear) of measurement, they are probably mean linear expansion coefficients over a range from room temperature to 400°C / 500°C. These data again indicate that, although both alkali-fluxed and lead-fluxed glazes have firing temperatures well matched to earthenware clay, the alkali-fluxed glazes have much higher thermal expansion coefficients and so are more likely to craze.

A more elastic glaze is more resistant to crazing and the elasticity, or Young's modulus, of a glaze is also governed by its composition. Thinner glazes are also less likely to craze than thick ones. Lastly, the homogeneity of the glaze is influential as large inclusions or bubbles can generate high, localised stresses, encouraging the propagation of cracks and so potentially worsening crazing.

Clay properties

The thermal expansion coefficients of clays are dependent on a variety of factors, principal among them being the clay mineralogy. Mineral inclusions with high thermal expansion coefficients over the temperature range 0–600°C, such as quartz and cristobalite, have a great effect on the overall thermal expansion coefficient. Therefore quartz or cristobalite are often added to clay bodies in order to counteract crazing (Grimshaw and Searle 1971; Hamer and Hamer 1997). Lime-rich clays often have high thermal expansion coefficients (Caiger-Smith 1973; Tite and Maniatis 1975) due to reactions involving lime (Peters and Iberg 1978; Bell 1965), although the influence of the rest of the clay mineral assemblage must still be taken into account.

Glaze / clay interface

The extent of the interaction between glaze and clay plays a large part in determining the severity of crazing. Interaction is influenced by factors such as the temperature and duration of the firing cycle and the chemical composition of both the glaze and clay. These parameters affect the viscosity of the glaze, how the glaze wets the clay, the rate of dissolution of the clay within the glaze and the type, quantity, and distribution of the phases that develop in the interaction zone.

The interaction zone often has a complex composite microstructure incorporating crystalline material, partially dissolved particles and bubbles in a glassy matrix. The presence of crystalline phases can have an extreme effect on the properties of a glassy material, even resulting in a zero or negative thermal

Table 6: Linear thermal expansion coefficients of different glazes

Composition	**T. Exp. Coeff.**	**T. Range**	**Reference**
SiO_2 73%, Na_2O 18%, CaO 9%	9.8×10^{-6} °C^{-1}	0-400 °C	Clarke 1966
"Alkali glass"	9×10^{-6} °C^{-1}	Unknown	Grimshaw and Searle 1971
SiO_2 73%, Na_2O 15%, CaO 7%, Al_2O_3 1%, MgO 4%	9×10^{-6} °C^{-1}	Unknown	Tite et al. 1998
SiO_2 80%, Na_2O 20%	9.5×10^{-6} °C^{-1}	Unknown	Tite et al. 1998
"High lead glaze"	5.5×10^{-6} °C^{-1}	Unknown	Tite et al. 1998
"Typical earthenware glaze"	6.4×10^{-6} °C^{-1}	Unknown	Singer and German 1960
"Typical earthenware glaze"	$3\text{-}7 \times 10^{-6}$ °C^{-1}	0-500 °C	Tite et al. 1998

expansion coefficient. The layers in the interaction zone are likely to have thermal expansion coefficients somewhere between those of the clay and the glaze. The resulting gradation in thermal expansion coefficient across the interaction zone, as opposed to a sharp discontinuity if the interaction were minimal, reduces crazing. The interaction zone may also be tougher than the rest of the glaze, as the presence of tiny bubbles and crystals and gradations in the glaze composition and properties may inhibit crack growth.

Glazing Egyptian and Mesopotamian clays

A glaze was replicated with a composition similar to that of ancient alkali glazes: 62.9 wt% SiO_2, 2.7 wt% Al_2O_3, 2.4 wt% FeO, 3.8 wt% MgO, 6.6 wt% CaO, 4.4 wt% K_2O, 15.1 wt% Na_2O and 2.0 wt% CuO. The glaze had a predicted thermal expansion coefficient of approximately 11.0×10^{-6}°C^{-1}, from literature data for comparable glazes. Raw materials were sieved together through a 250 microns mesh sieve and heated in crucibles in a muffle kiln at 2°C/min to 850°C with a dwell time of one hour. The resulting glassy material was ground in a ball mill, passed through a 250 microns mesh sieve and made into a suspension with water and gum Arabic. The suspension was applied to test tiles made from different clay substrates using a brush, dried and then fired. A firing rate of 2°C / min to 1000°C with a dwell time of 30 minutes was sufficient to produce a homogeneous glaze. Samples were taken from the test tiles and mounted in resin for examination and analysis with the SEM and WDS / EDS.

A variety of clay substrates were glazed (Paynter 2001), both pre-fired and unfired tiles, but only the results for pre-fired tiles are presented here. Similar interaction zone microstructures developed between the glaze and the unfired substrates, although the interaction zone tended to be further developed, and similar trends in the severity of crazing were observed. The samples labelled Eg or Ir were ceramic substrates cut from ancient Egyptian and Mesopotamian fired clay artefacts. The Red clay was obtained from a pottery supplier and the Gault clay directly from a quarry in Kent. The thermal expansion coefficients of the different clay substrates were determined using dilatometry by Marius Vendrell-Saz at the Departament de Crystallografia i Mineralogia, Facultat de Geologia, Universitat de Barcelona, for a heating and cooling rate of 3°C / min to 1000°C. The chemical compositions of the clays were determined using EDS analysis.

The severity of glaze crazing varied depending on the type of clay substrate. Figure 6 shows the replicate glaze applied to three samples of clay from artefacts:

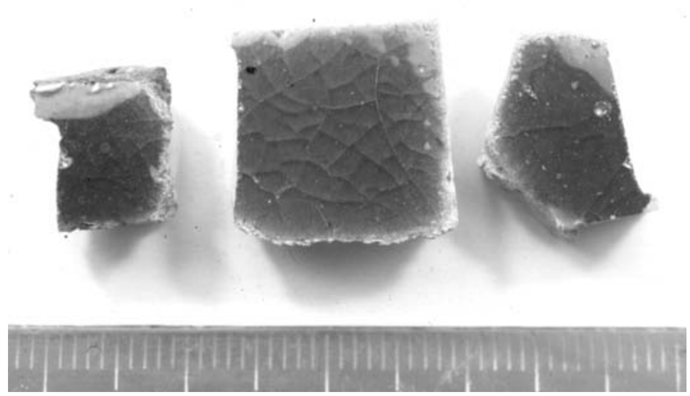


Figure 6: Replicate alkali glaze applied to (from left to right) Egyptian Nile silt clay (low lime and magnesia), Egyptian marl clay (lime-rich, low magnesia) and Mesopotamian alluvial clay (lime- and magnesia-rich).

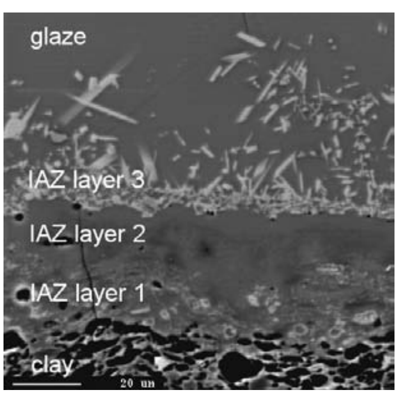
the Egyptian Nile silt (left), an Egyptian marl clay (middle) and a Mesopotamian alluvial clay (right). The crazing of the glaze on the Nile silt was the most severe, crazing on the Egyptian marl was of intermediate severity and crazing on the Mesopotamian alluvial clay was the least severe, and didn't occur until after the sample was removed from the kiln. The severity of crazing was evaluated using a three point scale: a ranking of 1 indicates very little, or no, crazing, 2 intermediate crazing and 3 severe crazing. Table 7 compares the clay thermal expansion coefficients over the temperature range 0 to 550°C and the clay compositions are compared for the different types of clay substrate glazed. The Egyptian marl clay and Mesopotamian alluvial clay have similar thermal expansion coefficients and therefore an additional factor must also be influencing crazing.

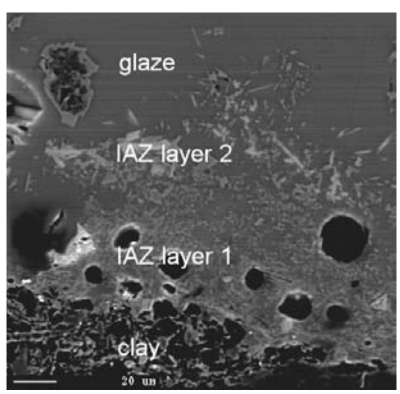
In terms of their microstructures, all of the glazes were identical regardless of the substrate to which they were applied, with the exception of the interaction zone, and it is this that has influenced the severity of crazing. SEM examination of the glazed samples showed that a more substantial interaction zone developed between glaze and clay when the clay contained more alkali earths (MgO and CaO), and this reduced crazing in the glaze. The correlation between the alkali earth content of the different clays and crazing can be seen in Table 7. The formation of the interaction zone is described in detail elsewhere (Paynter 2001) but is summarised briefly for different clay types below.

High lime, low magnesia: The high lime content of the Gault and Egyptian marl clays led to a complex interaction zone developing. The Gault clay also contained more alumina than typical of many of the other clays, which affected the microstructure of the interaction zone formed (shown in Figure 7). The interaction zone essentially comprised three layers: (1) a layer of partially dissolved clay (~20 microns thick) with some sub-micron wollastonite $Ca[SiO_3]$ crystals; (2) a distinct layer of alumina-rich glass containing no crystalline material (~15 microns thick) and (3) a layer of larger wollastonite crystals (white, needle-shaped). Increasing the firing time or temperature, or using an unfired (rather than pre-fired) test tile, led to this interaction zone becoming more developed with each layer thicker and better defined. The interaction zone microstructure for the Egyptian marl clay was similar but the layer of alumina-rich glass was absent.

Low lime, low magnesia: The red clay and Nile silt contained very little lime or magnesia and therefore no significant interaction zone formed (Fig. 9). Glaze / clay interaction was limited to a layer (~ 15 microns thick) where the glaze had penetrated into the body, some of the clay dissolved and an area of alumina-enriched glaze formed at the interface.

High lime, high magnesia: With the alluvial Mesopotamian clay, the presence of magnesia in addition to lime led to the formation of different crystalline phases (Fig. 8). In layer 1 (~ 50 microns thick) of the interaction zone, the glaze had penetrated into the clay body and partially dissolved the clay. This layer contained many tiny crystals (mid-grey in the image), which appear to be complex silicates such as augite $(Ca,Mg,Fe^{2+},Al)_2(Si,Al)_2O_6$. Layer 2 consisted of larger diopside $Ca(Mg,Fe)[Si_2O_6]$ crystals (mid-grey), with occasional wollastonite crystals (lighter grey).





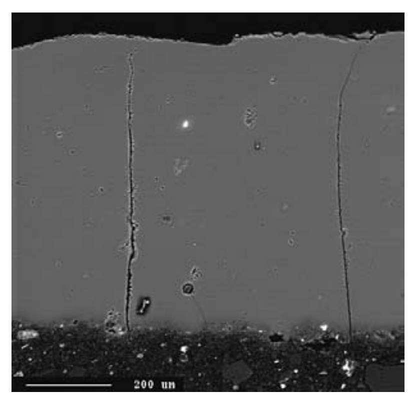


Figure 7 (left): Back-scattered electron image of interaction zone between clay and glaze on a high lime, low magnesia clay (Gault).
Figure 8 (middle): Back-scattered electron image of interaction zone between clay and glaze on a lime- and magnesia-rich clay (Mesopotomian alluvial).
Figure 9 (right): Back-scattered electron image of interaction zone between clay and glaze on a low lime and magnesia clay (Red).

Table 7: Effect of clay thermal expansion coefficient and composition on crazing

Clay	Description	Crazing Severity	T.Exp.Coeff. ($x10^{-6}$ °C^{-1})	CaO (wt%)	MgO (wt%)
Eg5b	Egyptian Nile silt	3	6.1	3.0	2.1
Eg7i	Egyptian intermediate	3	6.8	7.5	2.0
Gault	Kent	1-2	7.0	17.5	1.7
Eg7h	Egyptian Nile silt	3	7.1	2.1	2.0
Eg5a	Egyptian intermediate	2	7.7	9.1	1.8
Red	Potclays Ltd	3	8.0	0.5	1.0
Eg7p	Egyptian marl	1-2	8.8	12.9	3.1
Ir7a	Mesopotamian alluvial	1	8.9	12.4	6.6

Summary

In this study the properties of Mesopotamian alluvial clay were compared with different types of Egyptian clay, including lime-rich marl and low-lime Nile silt, and the compatibility of these clays with alkali glazes was evaluated experimentally. The alluvial Mesopotamian clay was found to be most suitable for use with alkali glazes, because it had a high thermal expansion coefficient and also high concentrations of lime and magnesia, which contributed to the development of a complex interaction zone, reducing the severity of glaze crazing. The clay also fired to a light colour, suitable for displaying a coloured glaze. The Egyptian marl clay, also light coloured, again had a high thermal expansion coefficient and contained high levels of lime. However this clay contained little magnesia and so the interaction zone formed was slightly less effective at reducing crazing. In contrast the Egyptian Nile silt was very unsuitable for glazing with an alkali glaze, as the clay contained little lime or magnesia and had a low thermal expansion coefficient, resulting in a severely crazed glaze. The clay also fired to dark colour, causing the glaze above to appear discoloured. In summary, the Mesopotamian alluvial clay is well suited for glazing with alkali glazes, the Egyptian marl clay is marginally less so and the Nile silt is unsuitable.

There is ample evidence to suggest that Egyptian artisans were producing glass from the New Kingdom onwards, and were therefore familiar with the raw materials and processes involved in glass production, also necessary to glaze production (Shortland 2000; Rehren 1997). The appearance of glass on clay kilns, kiln furniture and crucibles would have been observed in the course of glass production. If clay had been sought for glazing in Egypt, a pale coloured marl clay would probably have been selected and this type of clay has been found to be almost as suitable as Mesopotamian alluvial clay for glazing with an alkali glaze. The absence of glazed clay objects in Egypt cannot be satisfactorily explained by the differences in available raw materials or by a lack of technical knowledge.

In Mesopotamia stone was a rare commodity, with the exception of limestone, and clay was used for most structures, including monumental ones such as palaces and ziggurats, as well as for statues and for figurines. Prior to the mid-2nd millennium BC these objects were decorated in a variety of ways using paint or clay slips. Glazing clay provided a means of giving figurines and architectural details such as nails, wall plaques and bricks, a shiny, hard wearing and brightly coloured appearance. In Mesopotamia, faience was used to produce objects such as amulets, pinheads, beads, and vessels and occasionally for inlay. Faience does not seem to have had the same strong associations with particular functions, such as votive objects, as in Egypt and from 1500 BC glazed clay, glass and frit were used to make many of these types of object, as well as for extensive architectural decoration.

In contrast stone was employed on a large scale in Egypt for monumental buildings, statuettes and other items. Limestone, sandstone, granite, alabaster (calcite), quartzite, basalt, breccia, diorite and marble were used and decorated with paint. Where a glassy surface was required on vessels, figurines or tiles, faience was used instead. Egyptian artisans were extremely skilled with faience and it was used for many applications associated with the gods and funerary practices, not just because of its material properties, but also because of its cultural associations with rebirth (Friedman 1998; Moorey 1994, and pers. comm; Roaf 1996; Lucas and Harris 1962), strongly reinforcing the preferences of Egyptian society for this traditional craft. Around the time when glass begins to be produced, additions were made to the

palette of colours and the range of glazing methods available in faience. Detailed designs in very bright colours on different coloured backgrounds could be represented using faience inlay. Therefore many of the aesthetic effects desired by Egyptian artisans could be achieved best in faience rather than glazed clay.

Therefore it is likely that the technology for glazing clay was not adopted in Egypt, as in Mesopotamia, because there was no demand for glazed clay objects. Factors such as the strong cultural associations of faience in Egypt and the established stone working traditions would have contributed to this. It is indicative of the lack of demand for glazed clay objects in Egypt that there are no known examples of glazed clay objects being imported from other areas. In contrast glass, stone, metals and frit / faience are known to have been brought to Egypt via trade or tribute from the Near East.

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Appendix

Table 9: WDS analyses of glaze 1930.16.3 (see also Paynter 2001).

Na_2O	MgO	Al_2O_3	SiO_2	PbO	K_2O	SnO_2	Sb_2O_3	CaO	TiO_2	MnO	FeO	CoO	CuO	Total
11.49	3.10	0.20	67.91	0.11	5.60	0.04	0.15	6.01	0.02	bd	0.24	bd	2.35	97.22
12.97	3.89	0.64	64.64	0.10	5.51	0.10	0.11	6.67	0.05	0.08	0.26	bd	3.17	98.19
12.48	3.88	0.80	65.01	0.08	5.70	bd	0.09	6.54	0.07	0.02	0.24	0.04	2.24	97.19
12.65	3.85	0.78	66.42	0.12	5.66	0.04	0.11	6.95	0.06	0.11	1.58	0.03	0.67	99.03
12.49	4.06	0.77	65.34	0.04	5.51	0.02	0.10	6.40	0.01	0.05	0.27	0.05	2.48	97.59
13.49	4.15	0.64	66.75	0.02	5.59	0.11	0.01	6.00	0.04	bd	0.20	0.01	3.04	110.05
14.18	3.91	0.54	68.50	bd	5.67	0.04	0.12	5.91	0.08	bd	0.18	0.04	2.74	101.91
12.43	4.05	0.82	67.11	bd	5.85	0.08	0.13	6.66	0.02	bd	0.21	0.01	1.81	99.18
14.47	3.80	0.62	66.86	bd	5.68	0.08	0.09	6.16	0.03	0.04	0.27	0.03	3.03	101.16

Table 10: WDS analyses of interaction zone glaze in sample 1931.1.162 (see also Paynter 2001).

Na_2O	MgO	Al_2O_3	SiO_2	PbO	K_2O	SnO_2	Sb_2O_3	CaO	TiO_2	MnO	FeO	CoO	CuO	Total
14.84	2.06	12.70	56.69	0.04	3.99	0.04	0.08	2.85	0.24	0.03	3.94	0.02	0.97	98.49
12.03	1.51	10.61	63.02	bd	4.71	0.01	0.12	2.25	0.24	0.02	2.88	0.01	0.76	98.17
13.75	2.43	8.17	63.13	bd	4.11	bd	0.10	3.40	0.18	0.04	2.37	0.01	0.98	98.67
12.01	1.94	6.96	64.28	bd	4.15	0.06	0.08	3.66	0.21	bd	2.79	0.04	0.86	97.04
13.80	2.45	5.49	64.10	bd	4.10	bd	0.10	3.68	0.18	0.02	2.96	0.05	1.17	98.41
10.98	2.74	4.23	68.63	0.24	4.13	bd	0.15	2.56	0.35	bd	4.07	0.01	0.46	98.55
13.02	2.60	8.98	62.94	0.02	4.17	bd	0.08	3.87	0.31	bd	2.72	0.03	1.33	100.07
13.04	2.00	7.45	67.36	0.02	4.57	bd	bd	3.50	0.24	bd	2.66	bd	0.80	101.64
11.49	2.36	9.38	65.46	bd	4.47	bd	0.03	3.13	0.30	bd	2.18	bd	0.80	99.60
14.01	1.91	10.60	62.85	bd	4.56	0.03	0.07	2.71	0.29	0.03	2.50	bd	0.85	100.41
12.85	2.30	9.38	63.85	0.06	4.32	bd	bd	3.24	0.24	bd	2.46	0.01	0.92	99.63
11.44	2.47	5.66	65.33	bd	4.23	bd	bd	3,61	0.15	bd	2.70	0.01	1.11	96.71
13.79	1.94	8.93	62.92	bd	4.59	bd	bd	2.53	0.34	bd	3.08	0.01	0.99	99.12
12.19	2.63	4.05	69.16	bd	4.30	bd	bd	2.64	0.15	bd	3.74	bd	0.60	99.46
10.15	2.85	3.85	68.50	0.02	4.28	bd	bd	2.79	0.28	bd	3.81	0.03	0.50	97.06

Note

1 English Heritage, Fort Cumberland, Portsmouth

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Chapter 10

The fish's tale: a foreign glassworker at Amarna?

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Abstract

The glass fish excavated in the city of Amarna in Middle Egypt is described and its significance assessed. The findspot of the fish within the city is re-examined and it is proposed that the fish and its associated objects represent a glassworker's cache, interred early on in the city's brief history. The associated objects include three that suggest that the glassworker may have been of Syrian origin, which represents the first archaeological evidence for foreign glassworkers working in Egypt, an idea that has long been thought a possibility.

Introduction

The polychrome glass fish from Amarna is one of the most well known ancient glass objects. It is a popular object in the displays of the British Museum (museum reference EA55193) and is frequently loaned to foreign exhibitions. It is pictured in many general publications on Egypt (Shaw and Nicholson 1995) and most books on the beginnings of glassmaking (Tait 1991; Nicholson 1993), where it represents one of the peaks of glassmaking skill, rightly being referred to as "the product of both tremendous technical skill and creative design genius" (Kozloff and Bryan 1992). It is probably the most photographed glass object before the Roman period and this is not surprising, since it is still an aesthetically pleasing design even to modern eyes. This paper reviews the history of the fish, looking at the location where it was found, its function and its possible symbolism. It goes on to incorporate recent research which sheds new light on the fish and the people who made it.

Findspot

The fish was found in the ancient city of Amarna in Middle Egypt (Peet and Woolley 1923). The city was the capital city of the king Akhenaten, who reigned from 1353–1336 BC (Shaw and Nicholson 1995). It was built on a virgin site and was largely abandoned soon after his death, hence all the finds on the site can be tightly dated to the middle or late fourteenth century BC. The city was first excavated by W.M.F. Petrie in the late nineteenth century (Petrie 1894), where he uncovered a series of glass and faience making workshops (Petrie 1894, 1909). From 1907 to 1914 the Deutsche Orient-Gesellschaft (DOG – German Oriental Society) excavated parts of the city (Borchardt 1907–14, 1980), but after the Great War the concession reverted to the British once again. From 1921 to 1936 the excavations were conducted by the Egypt Exploration Society (EES) under the direction of a series of scholars including Thomas Eric Peet, Leonard Woolley, Francis Newton, Henri Frankfort and J.D.S. Pendlebury. It was during these excavations in 1921 that the fish was discovered. The EES were excavating a group of houses at the very southern end of the Main City. They lay along a narrow street called "Street C" by the excavators. This street joined "Street A" to the West to "East Road South" also known as "High Priest Street" to the East (Peet and Woolley 1923; Kemp and Garfi 1993). These houses lay to the North of Street C, the houses to the South being largely destroyed by a watercourse.

The fish was found in house N49.20, about half

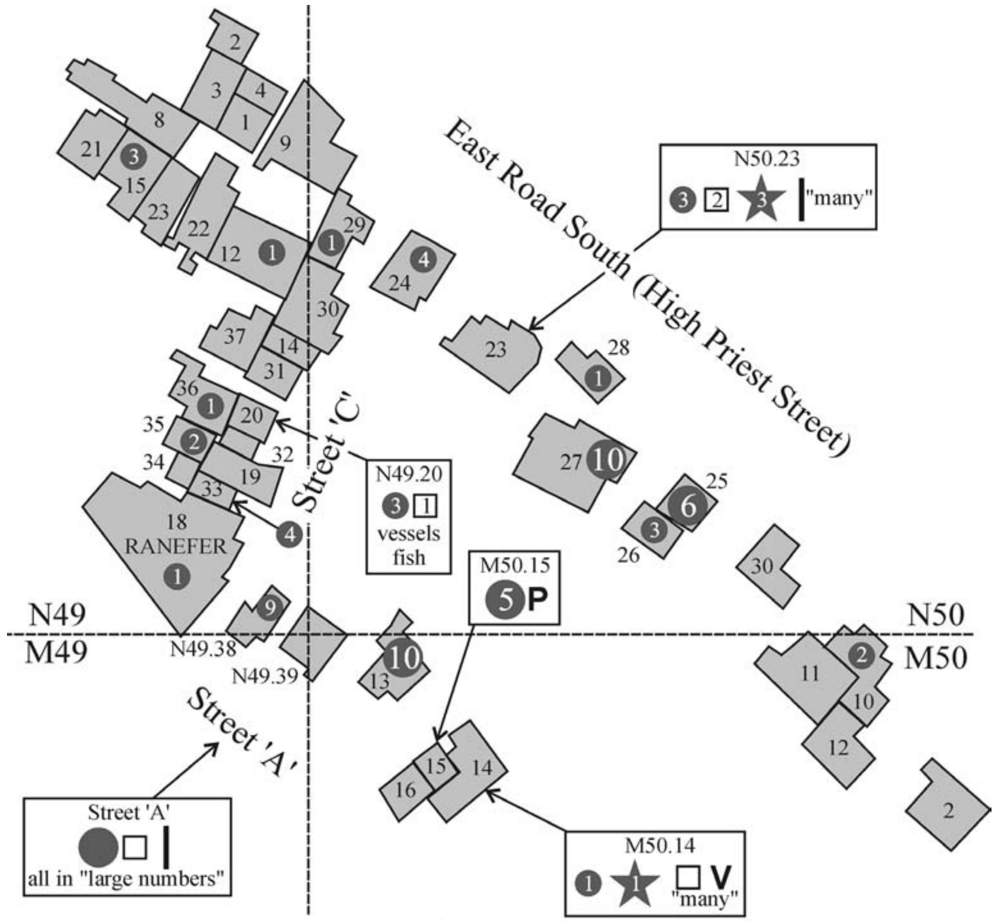

Figure 1: M50/N50 group, lying south of the Main City at Amarna, an area where glass and glaze making debris is particularly concentrated suggesting a workshop area (from Shortland 2000a). The numbers represents the number of certain glass and glaze making debris found in each of the houses: circle = faience moulds; star = kilns: rod = glass rods for trailing and marvering; square = "werkstück", a piece of discarded glass associated with glassworking; "V" = cylindrical vessels with tears of molten glass, probably some sort of crucible for glass melting or working.

way along Street C. Most of the houses in this area are very small and lightly built. A brief look at the initial descriptions given in the excavation monograph for the houses that surround N49.20 give a flavour for the area. N49.31 is a "poor house", N49.32 is "shapeless", others are "much ruined", "very small" and "unimportant" (Peet and Woolley 1923). The area is therefore one of little prestige, sandwiched between roads and more important houses, for example the house of Ranefer, the Master of the King's horses (N49.18). N49.20 appeared to the excavators to have "no entrance", from which they concluded that it had been architecturally altered several times (Peet and Woolley 1923). It had the foot of a well preserved staircase, showing that it had either two stories or, more likely, had a flat roof that was used for storage or accommodation. To the east of N49.20 was a group of outbuildings that had also been heavily reconstructed. At some point during its history, N49.20 was altered to turn the house into an open passageway running from Street C to the north, separating house N49.20 from N49.31 and N49.36 from N49.37. However, the basic plan of rooms remained, and it was in the southernmost of these "rooms" against the southern wall near the entrance that the fish was found (Peet and Woolley 1923). It was found in several fragments "under a double plaster floor", along with "two bottles of blue, yellow and white glass in ripple pattern…[and] three vases probably of lead… in poor condition… the L-shaped vase is open at both ends of the L, but it is difficult to imagine what was its use" (Peet and Woolley 1923).

Material

The fish is 14.5 cm long, 7 cm high and 3.2 cm wide at its widest point (Kozloff and Bryan 1992). In structure, the fish is a standard core formed glass vessel, but of modified shape and designed to sit on its side. The body glass of the fish is a mid to dark blue colour, and probably a cobalt blue opaque glass, although copper blue is also possible. The decoration of the fish's body consists of trailed and marvered glass mostly in white with a contrasting yellow trail every 3–5 white trails. The trails are dragged into a "U" shape finish so that they resemble fish scales. The tail consists of an extension of the body glass, so is of a similar colour, but here the opposite pattern to the body is used, the trailing being mostly yellow, with one white band. The eyes of the fish are made of spirals of black and white glass. A long streak of yellow beneath the eyes denotes the gill cover. The long dorsal fin is beautifully made from blue, white and yellow glass rods that have been skillfully laid together and partially melted to give a fluid effect. The pectoral fins are modeled with two blue glass rods each, and the ventral fins in yellow and white. The ventral fins have been greatly simplified and act as a base for the fish so that it sits upright when on a flat surface. In fact the fish would still have been very easy to knock over, suggesting that it probably at one time had a stand (Cooney 1976).

This fish is one of four glass fish known, two mostly complete and two fragmentary (Nolte 1968). A fragment of the tail "of an identical glass fish" was found at Malkata by the Metropolitan Museum of Art's excavations (Kozloff and Bryan 1992). This, along with stylistic and colour considerations, has led Kozloff and Bryan to suggest that the fish belongs to a group of glass vessels that were made at the glass workshops at Malkata, rather than Amarna. Wherever the British Museum fish was made, it is by far the most accomplished in terms of execution and design and none of the others have good provenance or dating evidence. No other animal form is known in glass vessels of this period.

Function

Most glass vessels of this period seem to have been in part functional objects, designed to contain another material. Some from their shape and still extent contents are obviously designed to hold the eye cosmetic kohl, usually a black powder made of galena (lead sulphide). This is especially clear when the glass vessels are skeuomorphs after kohl pots or kohl tubes of stone and wood, and in any cases evidence of traces of kohl are left in their bases. However, the vast majority of glass vessels are not obviously kohl pots (Nolte 1968) and another function has to be sought. The fact that glass vessels of this period are thought to be of great value (Nicholson 1993; Shortland 2000b), implies that their contents should have been valuable as well. From this conclusion, and their known association with cosmetics, the most likely content for these vessels is precious oils or perfumes. The shape of the fish, lying as it does on its side, presents a difficulty with this normal interpretation, since a non viscous liquid would have flowed out. It is probable that its primary role was never particularly functional.

Symbolism

The modeling of the glass fish is so good that it is possible to say for certain which species of fish the object represents. The fish represents the common Nile species *Tilapia nilotica,* a fish commonly represented in tomb paintings and in fish shaped cosmetic palettes. Also known as the bulti fish, it seems to have been a manifestation of the sun-god (Shaw and Nicholson 1995), perhaps because it keeps its fertilised eggs in its mouth until they hatch and then releases them giving the impression of live birth (Brewer and Friedman 1989). It is therefore perhaps a symbol of that most favourite of Egyptian preoccupations, rebirth and resurrection. As such they may have had a funerary use, and may have been connected with ritual anointing a statue or mummies. Eyepaints and ointments were essential to resurrection. Before appearing in the 'Hall of Justice' the individual had to purify her/himself, dress in white clothing, make up their eyes and anoint themselves. Applying eyepaint also seems to have been part of everyday cult rituals. Depictions of cows destined for ritual slaughter are sometimes shown wearing eyepaint (*www.swan.ac.uk/egypt/infosheet/fish.htm*). The bulti fish was also mentioned in medical papyri as an ingredient for the preparation of a salve.

Interpretation

One of the issues that has been brought out when considering the interpretation of the fish is its relationship to its find site. The fish is undoubtedly a high status object. Glass vessels at Amarna are most often found in the area of the Palace dumps, suggesting that their main use was by the court (Petrie 1894; Shortland 2000b). The artistic merit of the fish, plus its size, would suggest that if anything it was more valuable than the average glass vessel. How-

ever, the fish was found in an area of housing that is of very low status, under the floor of a "house" that was essentially only a thoroughfare to houses behind it. Cooney (1976) spotted this problem, and interprets the fish and the objects found with it as a cache that "may well represent the results of a robbery" late in the period of Amarna's history "when the future of the city was still [*sic*] uncertain". This is the normal explanation for the fish's presence in the house, but it does not fit well with all the facts. Firstly, the fish is found in a house that, to all intents and purposes is a corridor, hardly the safest place for burying a looted cache. Secondly, the fish was under *two* plaster floors, the suggestion implied by the excavators that at least the second was added *after* the fish had been buried (Peet and Woolley 1923; Griffiths 1926). Hence the floor was probably renewed after the cache was made. This all suggests that instead of being deposited late in Amarna's history, it is perhaps more likely that it is early, when the house it was deposited in was still a house and was actively being maintained. This makes it unlikely that it is a robber's cache. Further work (Shortland 2000a, 2000b) on the distribution of finds at Amarna have suggested another more likely alternative. The house lies within an area where glass and glaze workers worked and probably lived, termed "M50/N50 Group", shown in Figure 1 (Shortland 2000a). In this group of houses around four kilns, large numbers of glass rods, working pieces of glass, faience moulds and many cylindrical vessels for the melting of glass were excavated (Peet and Woolley 1923; Borchardt 1980). This suggests that the area was a production site for glass and glaze objects and that N49.20 fits into this group as potentially the residence of one of the workers in this facility. Therefore, perhaps the fish and objects associated with it are indeed a cache, but not that of a robber, but of a glass worker. This cache is likely to have been deposited early on in the history of Amarna, perhaps on the glassworker's arrival in the city or soon after.

This new context and slightly earlier date for the fish may also lead to explanation of its supposed Malkata influenced colour and style. When the glass workshops were first being set up at Amarna, the most likely place where the trained artisans would have been recruited from would have been the contemporary glass workshops at the Palace of Malkata. This is the only other known glass production site in Egypt at the period, and would have been very closely linked to Amarna through their strong royal connections. The first glassworkers therefore probably came from Malkata, bringing with them some of their tools, raw materials or ingots and perhaps some finished objects too. The reclassification of the fish to early in the history of Amarna means that it is possible that it was either brought with the Malkata glassworkers to Amarna as part of their stock, or was an early vessel made at Amarna using Malkata raw materials or ingots. Hence the redating of the fish helps explain why a Malkata-style object could have been found at a glass workshop in Amarna.

The second issue concerning the interpretation of the history of the fish concerns the objects that were found with it. The fish was found with two glass vessels, both single handled long necked vases (Nolte 1968: Taf. XIII.16 and XIII.18). These are quite unusual – only four glass vessels of this shape are known, and they fit in with the idea that this is a glassworker's hoard. However, of much more interest and significance are the other three objects found with these vessels (Figure 2). All were made of metal, probably lead. One of these objects is a one handled jug, one a small sieve and the third an L-shaped tube with a decorated supporting crossbar. It is clear that the excavators did not know what they were and beyond describing them, they did not venture any further interpretation. However, F.L. Griffiths (1926) soon realized what they were. The three objects represent part of a drinking siphon, a long straw being added to join the sieve and the L-shaped tube and a second straw running from the tube to the mouth. Interestingly, a stela (Berlin 14122, see Figure 3), also from

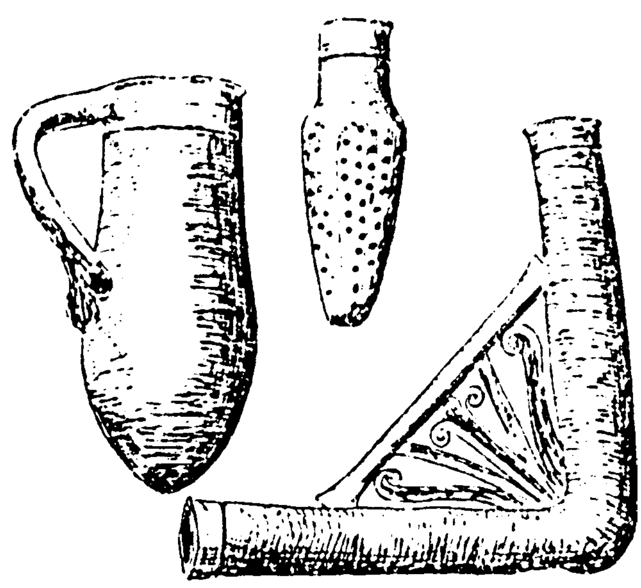

Figure 2: Metal siphon found with the glass fish at Amarna (from Griffiths 1926: Figure 1).

Figure 3: Stela from Amarna showing a Syrian mercenary using a siphon identical to that in Figure 2 (from Sparks 2004: Figure 3.4a).

Amarna, depicts just such a siphon in operation (Brovarski et al. 1982; Sparks 2004). The stela shows a male, seated figure sucking on the siphon which is supported by a slave. A female figure, probably his wife, is seated in front of him. The male figure is bearded and wears a hair fillet and polychrome kilt, all of which mark him out as a foreigner, specifically a Syrian. The spear propped behind his chair suggests that he is a soldier, probably a Syrian mercenary in Egyptian service. Drinking through a straw and filter was a Mesopotamian practice and common to both men and women and often shown on cylinder seals. It was introduced to Egypt during the New Kingdom along with foreign workers. However, as Sparks (2004) says, "Egyptians are almost never depicted using drinking straws themselves, and as finds of the associated fittings remain in the minority, it seems probable that this practice was never widely adopted in Egypt, and thus may have continued to be indicative of Asiatics". Thus the presence of this metal siphon with the glass vessels hints at the ethnicity of the glassworker who buried them both there. It suggests that he may have been a native of Mesopotamia or, if not a native himself, then strongly influenced by Mesopotamian ways of doing things.

It is accepted that glassmaking began in Mesopotamia (Peltenburg 1987; Nicholson 1993) and that foreign workers in various trades were present in Egypt (Moorey 2001), but the presence of the siphon with the glass fish in N49.20 provides the first archaeological evidence that a glassworker at Amarna may have been a foreigner, and specifically a Syrian. This supports the complex pattern of trade in raw materials, glass ingots, finished objects and trained artisans which seems to be typical of the interaction of complex societies of the Near East in the Late Bronze Age. It may also indicate how glass technology was transferred between the different states – by the movement of a small number of specialists between the courts.

Conclusion

The glass fish found at Amarna by the EES expedition in the 1920s represents an art object of the first importance. It is also of great interest because its provenance is so well known. Originally interpreted as the result of a robbery, it seems more likely that the fish and the objects accompanying it form a glassworker's cache, deposited early in the history of the city of Amarna. The fish itself may have been made at Malkata, which is also the most likely place where the glassworkers of Amarna were working immediately prior to their removal to the newly constructed city. The drinking siphon found with the fish is a typically Asiatic object, and suggests that the glassworker may have been a Syrian rather than an Egyptian. This represents the first archaeological evidence that glassworkers may have traveled between courts in a similar way to other artisans, and may hint at how the innovation that is glass technology may have been transmitted throughout the Near East.

Note

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Ancient copper red glasses: investigation and analysis by microbeam techniques

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Abstract

Four ancient red glasses ranging from the 14th century BC to the 11th century AD have been studied by electron micro-beam methods, in order to ascertain the origins of their colours. Analytical transmission electron microscopy was the main tool employed, but scanning electron microscopy, electron spectroscopy and time-of-flight imaging secondary ion mass spectrometry were also used.

The red colours of two of the glasses, a mosaic tessera from Hadrian's Villa (Tivoli, Italy) and an ingot from Nimrud, Mesopotamia, are mainly attributed to light-scattering by particles of cuprite, Cu_2O. The principal scattering particles in the other two glass samples, a Byzantine tessera from a church at the Parthenon, Greece and a cane from Tell el Amarna, Egypt are sub-micron-sized colloids of metallic copper. All four glasses contain exsolved crystals of halite, NaCl and they also have other inhomogeneities. The halite crystals and other features are thought to have little effect on the coloration of the glasses but have potential implications for the investigation of early glass technology.

Our findings suggest that the copper red colorations achieved by ancient artisans are not attributable to any single mechanism of chromatic dispersion or absorption. In particular, the occurrence of primary cuprite particles on a sub-micron scale in the Tivoli sample suggests that the nature of the precipitated phase may not be always directly related to copper and lead contents, leading to some unpredictability in the final colour.

Introduction

Sometime in the late 1980s, Mike Tite recognised that transmission electron microscopy had significant potential in the investigation of early materials. In the course of establishing a project on the microscopy of ceramic bodies, he introduced two of the present authors, a colleague from his time at the University of Essex and a member of his staff at the British Museum. This introduction prompted an on-going collaboration on the microscopy of glazes and glasses and it is a pleasure to present this paper in his Festschrift.

The use of copper red as a pigment for the coloration of glass appears to originate at about the same time as the earliest glass vessels, in the Near East in around the sixteenth century BC (e.g. Vandiver 1982). Since that time, copper-coloured opaque red glass has been utilised more-or-less continuously in the production of vessels, beads and enamels. While the production of translucent ("ruby") copper red glass was very challenging to early glass makers, a translucent red effect was sometimes obtained by flashing a thin layer of opaque red glass onto a colourless glass substrate, as in the ecclesiastical glass windows of medieval Europe. Copper has also been widely used in the production of translucent red ceramic glazes, from Ming Dynasty China through to the modern period (Scott 1992). Virtually all red glass before the seventeenth century AD is based upon copper coloration, with the exception of a handful of

Roman glasses that were coloured by a dispersion of gold alloy colloids, such as the Lycurgus Cup (Barber and Freestone 1990).

Red glass has held a particular fascination for specialists in early glass technology, and there is a substantial literature on ancient red glass (summarised by Freestone et al. 2003). Red glass often has a special symbolic significance (e.g. Scott 1992; Ram and Prasad 1965), and has been used on objects of high status, such as Celtic enamelwork. Furthermore, the need to maintain reducing conditions in the production of copper red glass meant that even in modern times it has been considered the most challenging of coloured glasses (Weyl 1951), and it tends to occur less frequently than other colours. Thus it is likely to have been a relatively rare and valued commodity.

The mechanism of colour generation in copper red glass and glaze has also been of interest to modern materials technologists, and there is a substantial body of published information on this subject, but surprisingly there has not been a clear consensus on the nature of the copper-rich phase responsible. It is clear that two phases, copper metal and cuprous oxide ("cuprite") can impart a red colour. Pettenkofer (1857) reported long ago that dendritic crystals of cuprous oxide were responsible for the red colour of some ancient glasses and this has been confirmed in later studies by X-ray diffraction of the bulk sample (Turner 1954; Bimson and Freestone 1985; Brill and Cahill 1988; Harding et al. 1989), while the presence of copper metal has been reported from other glasses (Brill and Cahill 1988; Bimson and Freestone 1985). Weyl (1951) claimed that coloration of copper ruby is always caused by a distribution of crystals of metallic copper, and this view has been widely held (e.g. Williams 1914). However, more recently red glaze and glass colours have been attributed to both metallic copper and cuprite in modern laboratory and industrial glasses (Ram and Prasad 1965; Bannerjee and Paul 1974; Paul 1982; Ishida et al. 1987; Wakamatsu et al. 1989). Similarly, while Cu-metal colloid particles are claimed to be the main source of coloration of Chinese ceramic glazes (Wood 1992), both Cu-metal particles (Freestone and Barber 1992) and cuprous oxide (Yusuke 1992) have been identified in such glazes, and both phases have been identified within the same glaze (Yusuke *op. cit.*), with indications that the state of oxidation varies with distance from the surface.

The identity of the particles that give colour in a particular glass is often not easy to prove: the sizes of particles and their distribution densities can vary widely, even within a sample; old coloured glasses can be inhomogeneous and it is common for there to be more than one second phase. The small sizes of the colourant particles usually necessitate the use of transmission electron microscopy (TEM) which can, however, bring its own problems (see below).

Brun et al. (1991) have studied a number of ancient red opaque glasses and enamels from France, using TEM. They reported the finding of mostly dendritic cuprous oxide in a Celtic enamel and mostly particles of copper metal in Gallo-Roman mosaic glass tesserae, although the two types of glass showed the presence of both phases. This is broadly consistent with compositional and morphological studies, which in general show that glasses such as Celtic enamel, with high lead contents (around 15 wt% PbO or greater) and high copper contents (c. 6 wt% or greater) contain dendritic crystals of cuprite, while glasses with low lead and low copper (typically around 5 wt% and 3 wt% respectively), such as the tesserae, contain sub-micrometre particles of a copper-rich phase, variously assumed to be either copper or cuprite (Hughes 1972; Bimson and Freestone 1985; Brill and Cahill 1988). The difficulties in identification of the fine particles in these earlier studies stemmed from the limitations of X-ray diffraction of bulk samples, where the abundance of the particles was near to or below the detection limits of the method and where both metal and oxide particles occurred in the same sample.

Microbeam instruments are valuable tools in the analysis of archaeological materials. Electron probe microanalysis and scanning electron microscopy are widely used (Tite 1992) but, as mentioned, TEM methods are currently the best means of proving the nature of the very small particles that generally occur in coloured glasses. Such particles are typically ~50–100 nm diameter and may be as small as 10–20 nm, as is stated to be the case of the metal colloids in silver and gold ruby red glasses (Bamford 1977; Volf 1984). Even TEM does not always give unequivocal results because of the possibility of phase changes or the breakdown of some mineral species during electron irradiation. In particular, halides (e.g. halite and fluorite) decompose readily and the tendency of cuprite to alter to metallic copper is a potential problem. The process of decomposition of cuprite under electron irradiation in TEM has been documented by Veblen and Post (1983) using the fibrous mineral variety called chalcotrichite.

The identification of early glass colourants is of interest in that it is a reflection of the raw materials, the *chaîne operatoire* and the choices made by the craftsperson. In this study we investigated four ancient glasses with a wide chronological and

geographical range, to determine the nature of the phases present and in particular to discriminate between the metallic and sub-oxide phases. Our aim was to evaluate the likely occurrence of the colourant species and whether there was significant variation worthy of more detailed study on materials of specific periods.

Glasses analysed

The glasses selected for analysis had been previously analysed by Freestone and co-workers using reflected light microscopy and scanning electron microscopy with energy dispersive X-ray analysis. Compositions determined by energy-dispersive X-ray analysis in the SEM are provided in Table 1.

1. Fragment of a plano-convex opaque red glass ingot from the Burnt Palace, Nimrud, Iraq (British Museum ANE 1957.2–9.10). Dated to 8–9th centuries BC. Analysis from Freestone (1988), previously discussed by Turner (1954), Bimson and Freestone (1985), Brill and Cahill (1987), Moorey (1994). This was selected because we can be confident that the colourant phase is cuprite. Essentially the type glass of the high-lead, high copper variety, containing about 4% antimony oxide, which may have been added to enhance the growth of cuprite. The base glass is soda-lime-silica with elevated potash and magnesia ("plant ash" type).
2. Opaque red mosaic tessera, Hadrian's Villa, Tivoli (BMRL 14122V). Second century AD. Low-lead, low-copper, soda-lime-silica glass fairly typical of the Roman period (previously unpublished).
3. Opaque red cylindrical cane from Tell el Amarna, Middle Egypt (British Museum AES 1934.8–16.193 or EA 67883). 18th Dynasty, Amarna period, *circa* 1340 BC. Analysis from Freestone (1987). Essentially no lead or antimony, but moderate amounts of copper. A soda-lime-silica glass with high potash and magnesia.
4. Opaque red mosaic tessera from the Byzantine church in the Parthenon, Athens (BMRL 33909V). 11th century AD. Low copper and very low lead (analysis from Freestone, Bowman and Stapleton forthcoming).

Table 1. Compositions of Opaque Red Glasses Examined.

	1	2	3	4
	Nimrud	Tivoli	Amarna	Parthenon
	1957.2-9.10	14122V	67883	33909V
SiO_2	42.28	58.39	59.58	66.1
Al_2O_3	0.68	2.69	0.47	1.7
FeO	0.43	0.99	0.36	2.2
MnO	bd	0.32	bd	0.9
MgO	2.84	0.85	3.32	1.4
CaO	3.82	6.56	8.87	6.7
Na_2O	9.46	16.28	17.15	14.8
K_2O	1.43	0.75	1.74	1.1
Cu_2O	8.58	2.87	5.18	2.5
PbO	24.96	6.44	bd	0.4
SnO_2	bd	bd	bd	bd
Sb_2O_3	4.19	0.73	bd	bd
SO_2	bd	0.85	0.17	0.2
Cl	0.45	0.88	1.10	1.0

Experimental methods

Small fragments of each glass were prepared as small-area thin sections; these were mounted on TEM support grids and ion-milled to perforation. We mostly cemented the pieces of thin section on carbon single-aperture-type grids to avoid possible sources of confusion when using analytical electron microscopy (ATEM). Ion-milling was completed at low angles of incidence (~10°), low kV (2–3) and low currents in order to minimise both surface relief and radiation damage. Beam milling of one glass (Hadrian's villa) initially introduced artefacts, which we soon suspected. In order to confirm that the results obtained from all the beam-milled specimens were reliable, additional specimens were made by crushing each of the glasses and mounting the resulting fragments between carbon-films supported by 200-mesh gold grids.

The analytical transmission electron microscopes used were a Philips CM20 equipped with a windowless energy dispersive X-ray (EDX) detector and a JEOL 200–CX fitted with a Be-window high angle X-ray detector. A JEOL 2010 high resolution instrument without EDX was also used on the Nimrud specimens. To analyse the small particles found in the glasses the microscopes were focused to give small probes, ~0.01–0.1 μm dia. Generally, we did not attempt quantitative analysis because of the

errors that would have been introduced because most particles were partially or completely embedded within the glasses. The ATEM work was supported with optical microscopy and SEM, as necessary. Investigation of the Nimrud glass by X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) was carried out using a Physical Electronics PHI 5600 multitechnique surface analysis system. More extensive and revealing results on the Nimrud glass were obtained using a Physical Electronics PHI 7200 time-of-flight secondary ion mass spectrometry (ToF-SIMS) system with imaging capabilities.

Results

1. Nimrud

The glass from Nimrud (BM reg. no. ANE 1957.2–9.10) was the most thoroughly studied sample of the group. This was because initially we found it complex and difficult to characterise fully. Extensive dendritic formations of cuprite emerged as the most important feature of the glass. Figures 1(a) and (b) and (c) show the microstructure of the dendrites and glass. The two features seen in Fig. 1(a) must have been sections through the same dendrite, as they were in the same crystallographic orientation. Figure 1(b) illustrates part of a massive dendrite, exhibiting the fairly typical morphology of the rounded ends of the branches. Figures 1(c) is the zone axis electron diffraction pattern corresponding to Fig. 1(a).

The cuprite readily decomposes during observation by TEM. The incipient alteration is apparent in the images of Fig. 1(a) and (b). After exposures to the beam of a few seconds the alteration causes the electron diffraction patterns to develop reflections that are indicative of copper. At first the electron damage led to some confusion about the nature of the dendrite-like growths and other particles closely associated with them. We resolved this problem in several ways. One was to study specimens of cuprite mineral in the TEM, so that we were better able to recognise the characteristics of cuprite, despite its tendency to alter to copper during electron irradiation. We worked mostly on cuprite sample no. BM72066 from the Natural History Museum, London.

Results from EDX microanalysis were somewhat equivocal because the dendrites of second phase and

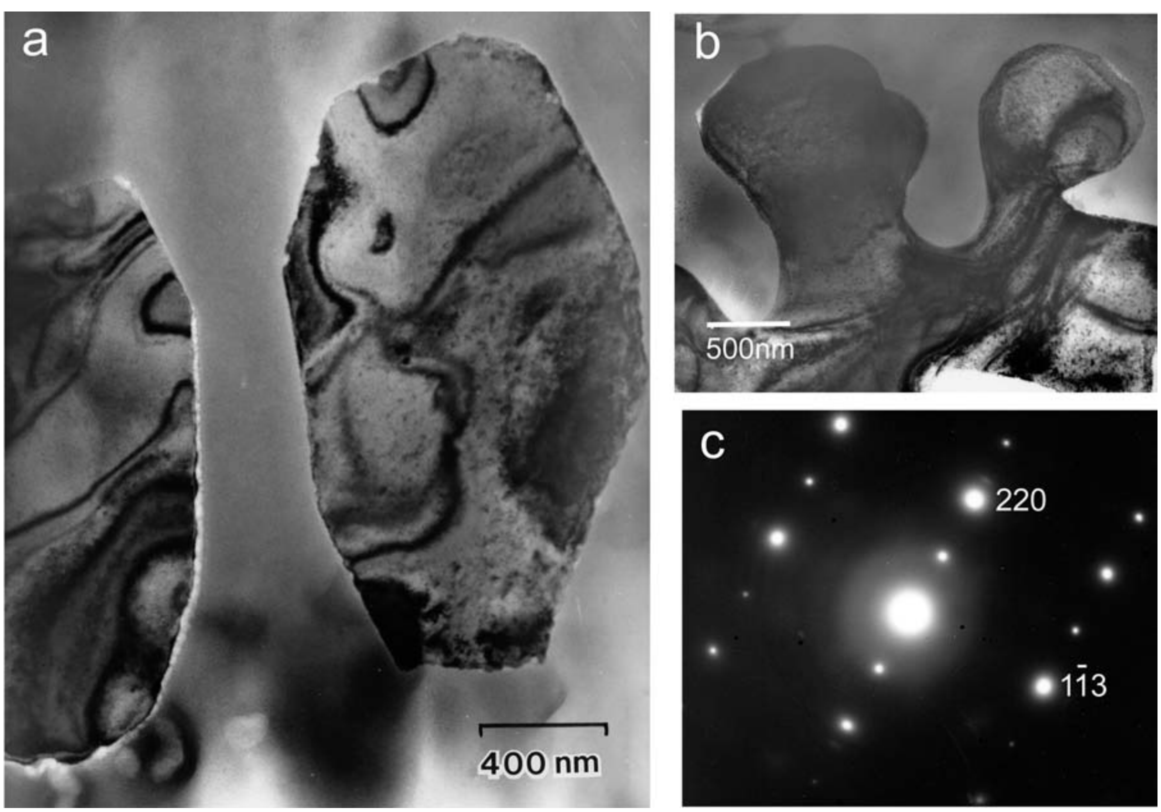

Figure 1: (a) and (b) are bright field TEM images of parts of cuprite dendrites in the glass from Nimrud. Some electron damage is apparent. Fig. 1 (c) is a selected area diffraction pattern from one of the dendrite arms seen in Fig. 1(a).

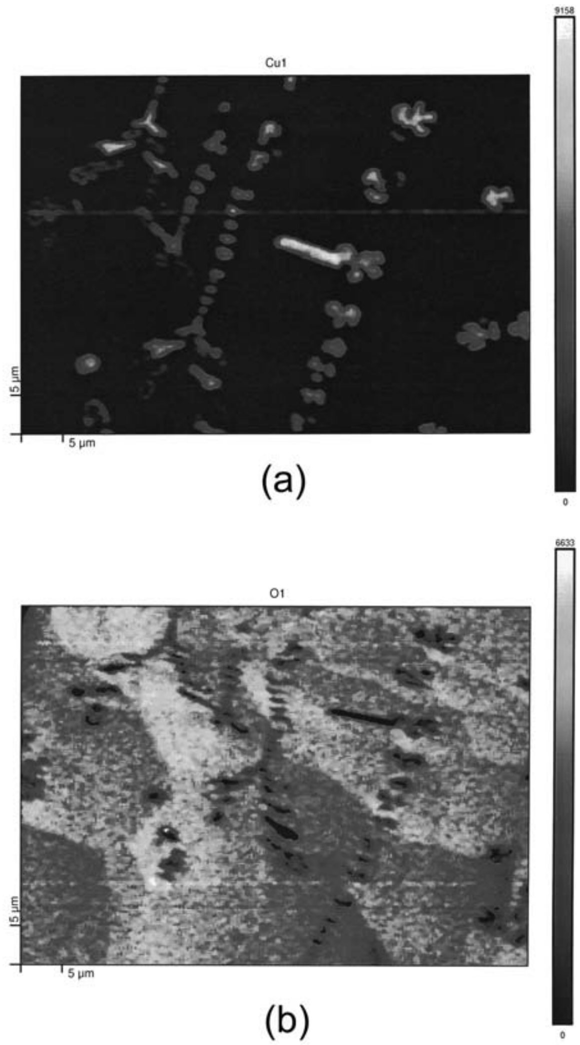

Figure 2: (a) An Auger electron map for copper (568 eV, L3M45M45 line), showing that the dendrites in Nimrud glass are rich in metal. Together with corresponding electron maps for oxygen (978 eV, KL23L23 line), which show that the dendrites contain oxygen, although proportionately less than the glass, e.g. Fig. (b), Auger mapping indicated that the dendrites are principally an oxide of copper.

individual crystals were usually still partially embedded in the matrix glass after ion-milling. As a consequence, nearly all microanalysis results from AEM have a spectral contribution from the surrounding glass and one cannot be sure of the source of the oxygen signal in the spectrum. We therefore carried out microanalyses using XPS, AES and ToF-SIMS, using equipment that enabled glass to be sputtered away to expose dendrites.

The XPS results show that the Nimrud glass contains the elements Mg, F, P, Cl, K, Ca, Cu, and Zn, in addition to Na, Pb, Si and O. There is also an indication of the possible presence of As. The overlapping of peaks is a problem, and some peaks could not be identified (e.g. one occurring at 555 eV). Auger-electron mapping of copper, Fig. 2(a), and oxygen, Fig. 2(b), suggests that both elements are present in the dendritic growths within the glass. The curve-fitting of the XPS lines for copper indicate that Cu is present in both metallic form (932.8 eV experimentally, cf. 933 eV) and as Cu_2O (932.0 eV experimentally, cf. 932.5 eV). The curve-fitting of three lines for oxygen indicate its binding into SiO_2 molecules and at least one other oxide, most probably Cu_2O.

The first results of the ToF-SIMS work were somewhat confusing in that many unsuspected impurities were identified. Consequently SIMS was not helpful in resolving our early question as to whether cuprite and/or copper should be identified with copper red. The answer was therefore pursued using TEM lattice imaging and electron diffraction. Subsequently, ToF-SIMS was used to greater effect and the results are summarised at the end of this section.

When lattice imaging was applied to Nimrud specimens using the JEOL 2010, it was apparent that the copper-bearing phase was very prone to radiation damage. Not only were the diffraction patterns seen to change, but also the nucleation of new crystallites was observed within the phase. Figure 3 shows a high resolution image obtained soon after decomposition commenced. The image exhibits {111} lattice fringes

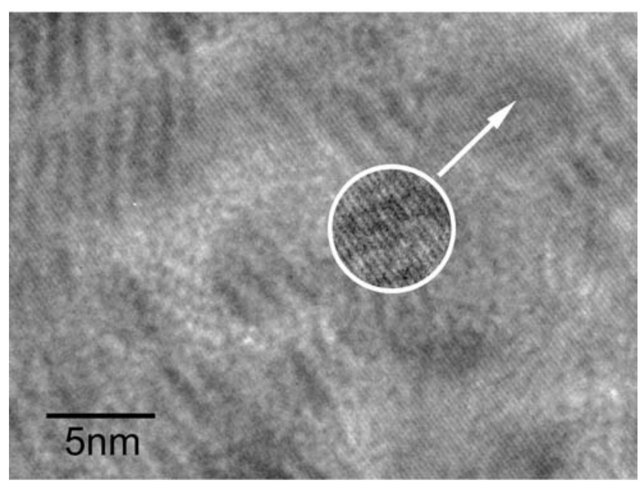

Figure 3: TEM lattice image from part of a cuprite dendrite in the Nimrud glass, showing incipient decomposition to copper. This is apparent as small islands with moiré fringes caused by the superposition of the two lattices with different lattice parameters. The lattice fringes, enlarged for greater visibility in the circular inset, correspond to the 0.25 nm spacing of the {111} planes of cuprite.

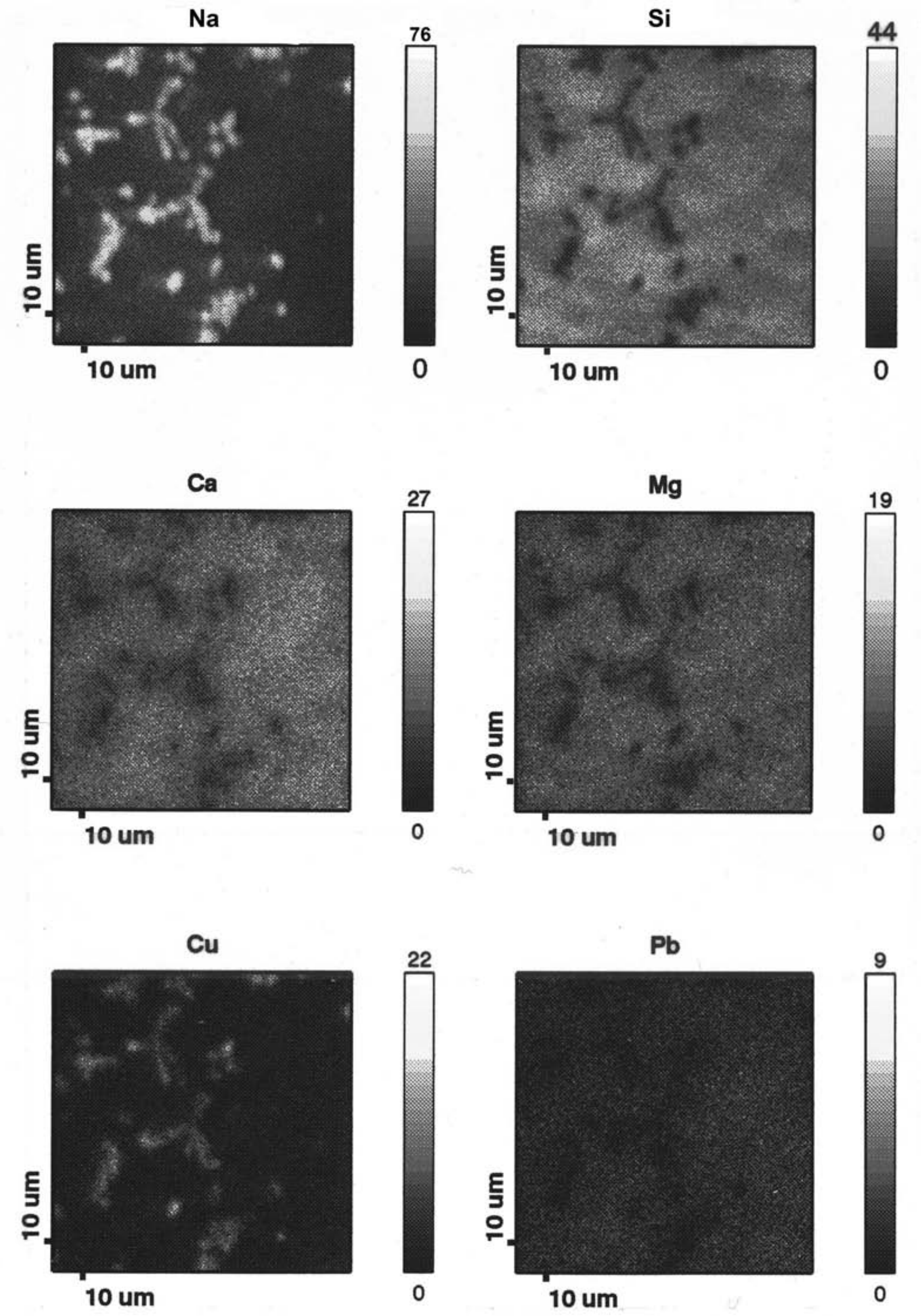

Figure 4: ToF-SIMS images from a Nimrud sample, illustrating the rejection of silicon and several other metals by the cuprite dendrites, but a surprising and unexplained affinity for sodium.

for cuprite and reveals small copper-rich rounded regions with moiré fringes. Diffraction patterns obtained from the original second phase (the dendrites) under minimum dose conditions (Williams and Fisher 1970), however, could invariably be indexed as cuprite. Therefore we are convinced that this is the phase that was originally formed within the glass during its heat treatment. In our experience the morphology and the decomposition of exsolved cuprite is distinctive and the characteristics of

precipitated cuprite in glasses differ substantially from those of copper when it is the exsolved phase.

Analysis by ToF-SIMS, before and after sputtering the polished surface, produced both anticipated and surprising results. The former include the detection of Mg, K, Ca and Pb in the glass matrix but not in the cuprite, these metals having been rejected from the dendrites during their growth. Positive mode SIMS results also show that lanthanides of masses 63/65 (Eu and Tb), detected at the 1 ppm level by ICP-MS, were strongly associated with the dendrites, which is consistent with the chalcophile properties of these elements. The elements Al and Sn are evenly distributed, i.e. they must be in solution in the dendrites. However, mass 32 (Cl, O_2/S) and mass Cu are strongly associated with the dendrites. Comparison of spectra and images obtained before and after a long sputter-erosion of the polished surface led to the unexpected conclusion that a compound with mass 26 occurred as a coating or surface enrichment of the dendrites. The mass 26 signal disappeared when the interior regions of dendrites were probed and analysed. This result is puzzling since mass 26 is normally attributed to CN whose presence, even at the low level indicated, is highly unlikely unless through some unknown weathering process. Some of these results are illustrated in the SIMS images presented in Fig. 4.

2. Hadrian's Villa – Tivoli

The first ion-milled specimens that we made from the Tivoli sample (BMRL 14122V) were very heterogeneous and it was suspected that the glass had been damaged by the milling. No particles of cuprite or copper, or any other anticipated source of coloration were identified unequivocally. There were, however, clumps of particles and some individual particles within the glass. Many of these were analysed. Their constituents varied somewhat; the most common X-ray peaks generated by the particles were those of Na, Al, Cl, S, and Fe, with smaller signals from Cr, Cu and Ni. From a comparison study on fragments formed by crushing and grinding some of the Tivoli glass, we soon concluded that with the exception of some Na, S, Cl, Ca and Cu, the impurities had been introduced during specimen preparation. Some porosity in the glass and a defect in the ion-mill had combined to cause their introduction.

Investigation of the crushed glass showed that a common exsolved phase in the glass was NaCl. The base glass is relatively homogeneous (not phase separated). It gave strong X-ray peaks for Si, with minor Ca, and traces of S, Fe, and Cu. Few copper-rich particles were found in the limited areas that were thin enough to transmit electrons well. Another two specimens were then made by atom beam-milling (using a different machine from that employed for the first two specimens). The results from the new specimens confirmed the glass composition obtained from the thin areas of the crushed glass. In these specimens we found numerous crystalline particles and many of these were analysed. However, the particles were not uniformly distributed; volumes of a few cubic microns occurred without any Cu-rich particles but with NaCl precipitates. The heterogeneity was manifest macroscopically as swirls of different intensity of coloration in the glass.

Using a combination of electron diffraction and EDX microanalysis we identified many particles of cuprite and sodium chloride in the atom-milled specimens. Figure 5 shows a cuprite crystal with a characteristic polygonal outline. Some electron damage is again apparent. Almost all the crystals in the glass are about 100–200 nm dia., and many were established to be cuprite by electron diffraction and microanalysis. It was often difficult to obtain exactly orientated zone axis patterns from the crystals and to retain them during photographic exposure, because of thermal instability. For this reason we often recorded several patterns at different orientations from a given crystal to establish its identity, and for many particles the sequences of patterns showed increasing evidence of breakdown to copper.

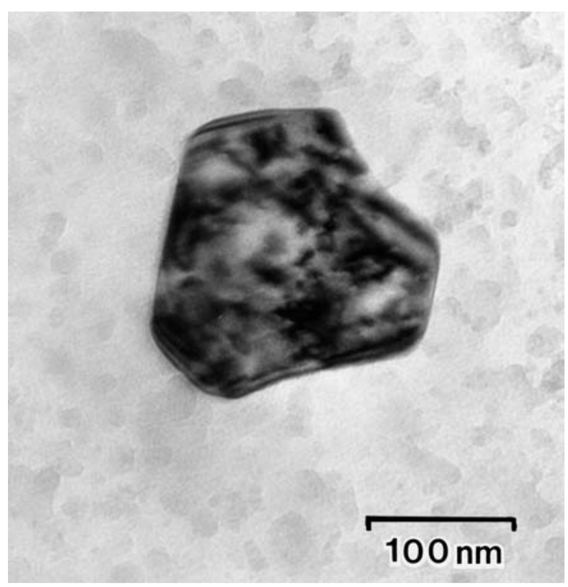

Figure 5: TEM image showing a cuprite particle in the glass from Hadrian's Villa, Tivoli. The viewing direction is almost along a <310> zone axis, with an 020 systematic row of reflections operating. The glass has a microstructure that suggests it is phase separated.

A few of the cuprite precipitates were considerably larger than those seen in Fig. 5, ranging up to 0.5 μm dia. Most particles were polyhedral in form and they were invariably single crystals. We suspect that some of the cuprite crystals may have been partially converted to copper *in situ*, prior to any exposure to electron irradiation. A low concentration of sulphur was invariably associated with the cuprite. The glass from Tivoli lacked any extensive or massive cuprite dendrites, which were prevalent in the Nimrud glass. The differences in the occurrences of cuprite in Nimrud and Tivoli glasses are attributed to the large differences in the concentrations of copper oxide and lead oxide (Table 1). Halite crystals were easy to recognize because of their tendency to decompose very rapidly under the action of the electron beam, leaving geometrically-shaped voids in the glass, unless care was taken.

3. Tell el Amarna

The matrix glass of the Egyptian sample is not phase-separated, but it is very inhomogeneous, with some optically-transparent dendrite-like growths and clustered particles, which are visible by optical microscopy. TEM shows that, most importantly, the glass contains small crystallites of Cu, about 200–500 nm dia. and typically ~10–100 μm apart. These are mostly slightly polygonal in form, the rest being more spherical. It is apparent from thickness fringes that most of the crystallites are un-twinned single crystals, typical examples being illustrated in Fig. 6(a). One of the crystals seen in Fig. 6(b) is a rare example that appears to be twinned. Sometimes the particles appear to possess a mottled microstructure, but after careful study we concluded that this is mostly due to glass lying above or beneath the particles, which tends to alter under electron irradiation. Figure 6(c) is a selected area diffraction pattern from an unusually large particle. For the average particle we used micro-diffraction. The diffraction patterns index as copper. Care was taken to use low electron beam currents to minimise irradiation and usually diffraction patterns were recorded from the particles immediately they were seen, before the corresponding images were recorded. In this way we could be certain that metallic copper had been precipitated in the glass, and not cuprite (as mentioned previously, this can become degraded to copper by the beam during observation). In fact the copper colloid crystals were very stable.

In addition to the copper particles, we also identified some of the other phases that were present, using a combination of microanalysis and electron diffraction. Exsolved particles of sodium chloride were the most numerous. Typically they are ~ 0.5μm in size and monocrystalline; their shapes are usually very geometrical and most conform to the outlines of cube-shaped crystals in various orientations. Particles that give X-ray peaks for Na and S are also quite common and these are probably sodium sulphate, which has been identified in other ancient glasses (e.g. from Hasanlu, Stapleton and Swanson 2002). Particles that contain Ca, Fe and Cu also occur (cf. Tivoli sample). We believe that these are iron sulphide (pyrite) and copper sulphides. The dendrites in this glass that are mentioned above appear to be a calcium silicate.

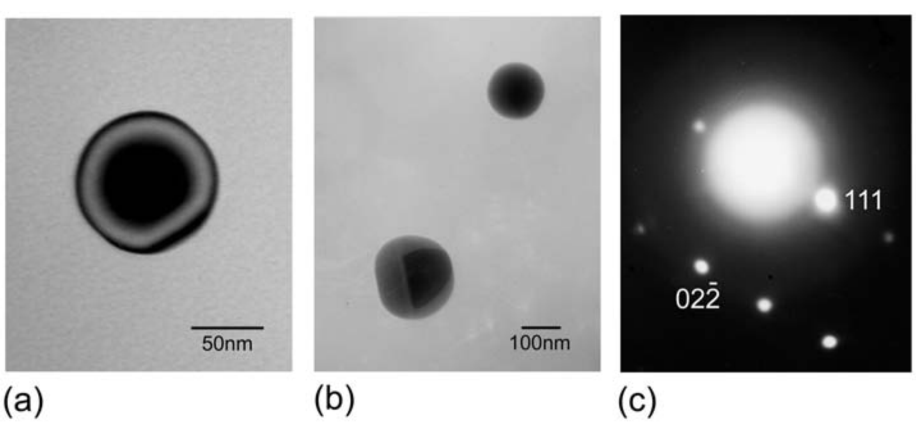

Figure 6: (a) and (b): TEM images of typical examples of copper crystals in the Tell el Amarna glass. Note in (a) the equal thickness fringes (caused by electron interference), which show that the particle is a single crystal and gives a feeling for its morphology. The slight mottling apparent on the particle is due to electron radiation damage to the embedding glass and possibly also to the metal. The two particles in (b) are unusually close together; the pattern of diffraction contrast in the larger one suggests the presence of a twin. Figure 6(c) is a selected area electron diffraction pattern obtained from a colloidal copper crystal of greater than average size.

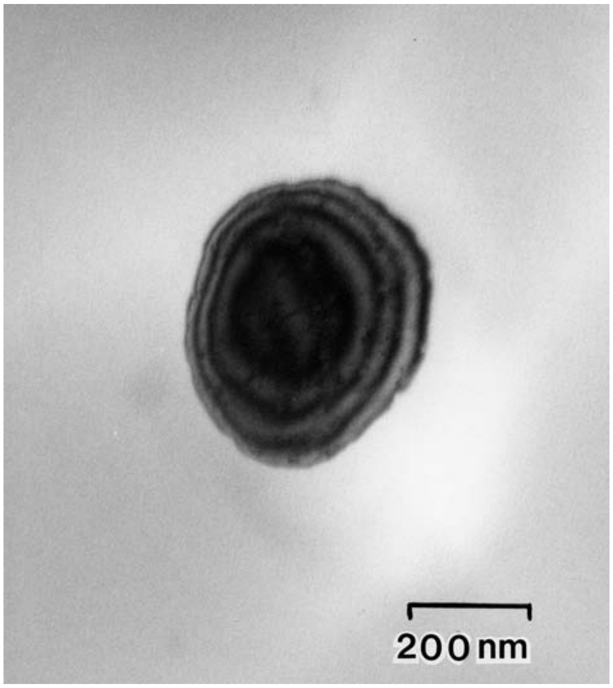

Figure 7: TEM image of a colloidal copper crystal in the glass from the Parthenon church, which bears close similarities to those illustrated in Figs. 6(a) and (b). The equal thickness fringes indicate that the particle is ovoid in shape; the operating reflection was 022.

4. Parthenon

The matrix glass from the Parthenon church is not single phase but is phase-separated (presumably due to metastable liquid-liquid immiscibility). We have not studied this effect in any detail.

There are two main types of particle in the glass from the Parthenon: exsolved metal colloids and exsolved halite crystals. In this respect the Parthenon glass is basically similar to the glass from Tell el Amarna (675533). The metallic and non-metallic particles have approximate size ranges from 50 nm to 200 nm and from 100 nm to 400 nm, respectively. The stability, morphologies and diffraction patterns of the metal colloids are consistent with them being copper, which contains small concentrations of Mn and Fe. The particles are generally rounded polygons in form and each is a single, untwinned crystal. Figure 7 shows a typical example of the copper crystals. As with sample 675533, we took care initially to minimise any possible radiation damage, in case we were also dealing with unstable phases, such as cuprite.

The halite particles in the Parthenon sample, like those in the Tell el Amarna glass, generally have more definite crystal faces than the copper colloids, although they degrade rapidly under the influence of a focused electron beam. The halite (NaCl) crystals mostly contain a low percentage (~ 2–5 wt%) of Fe and traces of sulphur are also common. Fig. 8(a) shows four examples; (b) and (c) are selected area diffraction patterns from two particles (the use of microdiffraction with NaCl causes rapid degradation

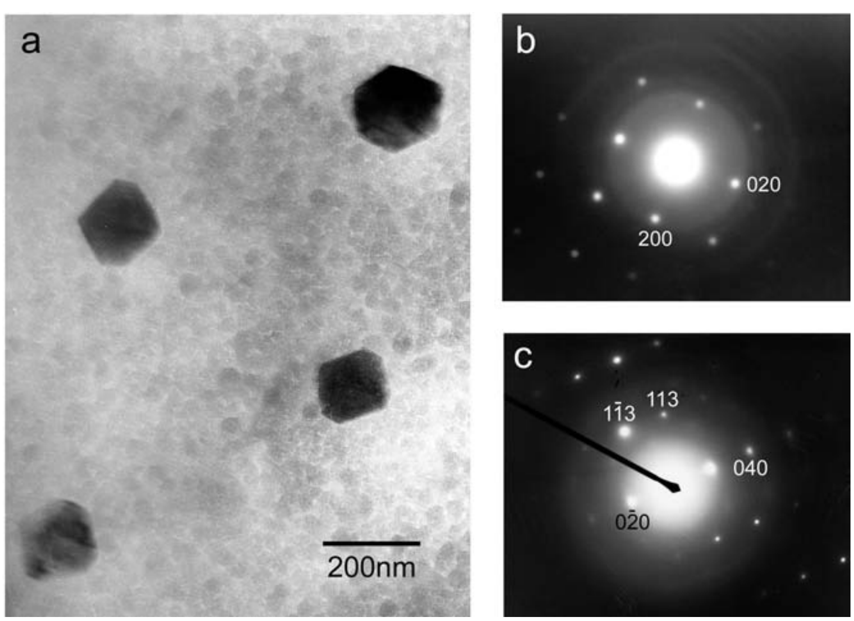

Figure 8: (a) TEM image of a group of typical halite (sodium chloride) crystals in the Parthenon glass which in this region appears to be phase separated; (b) and (c) are electron diffraction patterns from individual halite crystals.

and loss of sodium). We also found individual crystals that appear to be iron sulphide (probably pyrite) or possibly sulphate and some more massive K-feldspar.

Discussion

Origins of Colour

The four glass samples that we have studied all have red coloration, but two contain particles of metallic copper while the other two contain principally cuprite. Many exsolved NaCl (halite) particles also occur in the glasses, along with some other minor impurity phases, but none of these phases are thought to contribute significantly to the coloration.

The average distances between particles in the various samples can only be estimated roughly by TEM because no information about the third dimension is obtained. The average distance between particles in the essentially two-dimensional specimens of the Parthenon and Tell el Amarna glasses typically appears to be between 1 and 10 μm. However, the probability of the specimen plane passing through the small particles is low and the actual average spatial separation of the particles in these glasses is probably of the order of 500 nm. Cuprite crystals in Tivoli are typically separated by a few microns. The cuprite precipitates in Nimrud cannot be characterized in the same ways as the metallic-copper bearing glasses because of their dendritic morphologies.

The samples containing copper nano-sized particles owe their colour to the relative contributions of the incident light scattered and absorbed by the copper particles, the principles of which are discussed for example by Bamford (1977). The mechanism of coloration due to cuprite is likely to differ greatly from that of copper, at least in the Nimrud glass. Cuprite crystals in Nimrud are too large to be effective scatterers of light. Here, the coloration is due to the intrinsic colour (i.e. the absorption spectrum) of cuprite, which is a skeletal-type microstructure embedded in the colourless glass matrix.

It is surprising that the copper-rich nano-sized particles in the mosaic tessera from Tivoli are mainly of cuprite. It is unclear that colloidal cuprite and copper should yield the same colour. Furthermore, there are indications from observations on early glasses that fine cuprite particles impart a more yellow or orange colour to the glass (e.g. Cable and Smedley 1987). It may be that the red colour of this glass is due to contributions from both the cuprite and the subordinate copper particles.

Comparing our results with those of Brun et al. (1991) there is a level of consistency, in that all three glasses that they studied containing sub-micrometre particles appear to have been coloured by metallic copper, while two of the three glasses of this type that we studied were similar. However, precautions taken to prevent the decomposition of cuprite in the electron beam allowed us to identify common particles of cuprite in the glass from Tivoli. In order to understand this, it is necessary to consider the mechanisms of precipitation of copper and cuprite in the glasses.

Metallic copper is essentially insoluble in silicate melts and glasses. It was dissolved in the glass as copper oxide and precipitation was induced, for example, by heat treatment and/or adding carbon or iron, which reduced the oxide to metal. In this way, the formation of copper particles could be induced in glasses that contain one percent or less of copper. Indeed, excessive concentrations of copper would not have been helpful using such an approach, because particles would have grown too large, spoiling the colour. In contrast, as an oxide, Cu_2O is significantly more soluble. In order to induce the precipitation of cuprite, the glass melt was usually more-or-less saturated with high concentrations of Cu_2O, in the range 5–10%. The benefits of lead oxide are several, but it appears that this component shifts the CuO/Cu_2O equilibrium towards Cu_2O thus increasing the tendency of cuprite to crystallise (Edwards et al. 1977; see also Ahmed and Ashour 1984). Furthermore, according to the experiments of Williams (1914) on ruby glasses and by Ahmed and Ashour (1974) on cuprite reds, lead improves the rates of nucleation and growth.

Thus there exists in the behaviour of the glass melts an explanation for the compositional and microstructural contrasts between the two fundamental types of opaque red glass. Low-lead, low-copper glasses do not necessarily need lead, and require low levels of copper as they are generally coloured by copper metal nano-particles that are exsolved due to the reduction of the melt. High-lead, high-copper glasses require high copper oxide contents and high lead contents to promote the formation of cuprite; with too little copper, cuprite would be unlikely to form, while with too little lead, it would not form the dendritic structures which produce the brightest reds.

The glass from Tivoli is apparently an exception, as it is a low-copper, low-lead glass which precipitated nano-sized particles of cuprite, with subordinate copper. It is surprising that the 3% copper oxide in this glass was sufficient to cause cuprite to nucleate, in the presence of only 6.4% PbO (Table 1).

However, in principle, it is not impossible that under particular melting conditions this might occur. An alternative mechanism is suggested by the thermodynamic arguments of Paul (1982: 264) and also by Ishida et al. (1987), whereby the glass first nucleates copper then passes into the stability field of cuprite, causing co-precipitation of copper and cuprite, cuprite to precipitate on copper nuclei and possibly conversion of pre-formed copper into cuprite.

Sodium chloride and other exsolved phases

The transparency and other optical properties of halite do not make its presence easily detectable in glass by light-optical methods. NaCl crystals were also found in our earlier study of the glass of the Lycurgus Cup (Barber and Freestone 1990) and it seems likely that the exsolution of NaCl was an inevitable consequence of reheating the glasses to cause the colorant particles to strike. Chlorine was incorporated in virtually all soda-lime-silica glasses before the advent of the Solvay process in the nineteenth century, as it was added as a component of the plant ash or natron soda source. As we noted previously (Barber and Freestone 1991), when first made, glasses are likely to have been saturated with chloride, implying an initial concentration in the order of 1.42 wt%, as measured by Bateson and Turner (1939). A scum containing chlorides and other insoluble salts such as sulphates is likely to have formed on the surface of the melt. Evidence for this is found in the positive correlation of sodium and chlorine in ancient glass, noted by Wedepohl (2003), which suggests that the chlorine content is controlled by a solubility relationship. Measured chlorine concentrations in ancient soda-lime-silica glass are typically in the range of 0.6–1.4 wt%. There is a wide miscibility gap with a strong temperature dependence between liquid silicates and NaCl (Delitsyn and Melent'yev 1968) and in cooling a glass saturated with chlorine it would pass into the two-liquid field (exsolving a sodium chloride liquid) or into the stability field of crystalline sodium chloride itself. In the present case, the morphological evidence suggests that in general, crystals of sodium chloride have separated.

While we assume that in the glasses that we have studied, the sodium chloride separated during a heat treatment needed to separate the colourant phases, it is possible that sodium chloride has separated in many ancient glasses but has remained unnoticed. Examination of selected transparent glasses using TEM would be needed to investigate this possibility. This possibility is not merely of theoretical interest; it has implications for the weathering of glass and for the elemental analysis of glasses using microbeam techniques. The preparation of polished surfaces using aqueous polishing fluids could lead to the dissolution of sodium chloride particles and shortfalls in Na and Cl values.

The presence of sodium sulphate in some glasses is of similar significance to the sodium chloride, reflecting saturation in some components of the soda rich flux added to the batch, either plant ash or natron. The precipitation of iron sulphide particles, however, reflects in particular the reducing conditions that were necessary to produce copper reds and the existence of reduced sulphur in the melt. The observation that the glass from the Parthenon is phase-separated is also important, as we are not aware that this phenomenon has been previously reported from ancient glass. Once again it has implications for the environmental stability of the material, as the two phases are likely to show differential leaching characteristics.

The finding of the surface layer of mass number 26 on the cuprite dendrites in the Nimrud glass is enigmatic but gives an indication of the complex composition of the natent glass and the intricacies of the precipitation process. Very slow diffusion in glass is possible at ambient temperatures, so the enrichment probably occurred both by scavenging as the glass cooled and subsequent maturation. We do not know whether the finding would be general for cases of cuprite precipitation in glasses or whether it has some special significance. The oxide particles in the glass from Hadrian's Villa are too small for imaging by ToF-SIMS, which currently has a resolution limit of 0.5 μm. We feel that ToF-SIMS has promise as a possible technique for understanding the variations in processing of ancient glasses, although much more work would be needed before results could be fully interpreted.

Conclusions

Transmission electron microscopy has proven a very useful, perhaps definitive, technique for the investigation of the colourant phases in copper-red glasses, as long as care is taken to ensure that original cuprite does not decompose to metallic copper in the electron beam. As anticipated, the colourant in the high-lead, high-copper opaque red glass from Nimrud was found to be cuprite, Cu_2O. The colourant in two of the three low-lead, low-copper glasses was found to be sub-micron particles of metallic copper, but unexpectedly the principle colourant phase in a tessera from Tivoli was found to be sub-micron

particles of cuprite. However, this is consistent with previous reports of the coexistence of copper and cuprite in this type of glass, based upon X-ray diffraction of bulk samples (Brill and Cahill 1988).

The occurrence of the two phases is explained by the existence of two distinct approaches to the production of opaque red glass. One approach involved the addition of high levels of lead and copper to a base glass, which favoured the nucleation and growth of cuprite, often producing large dendritic crystals. The other involved the presence of relatively low quantities of copper in the base glass, with or without lead, and depended upon the addition of reducing agents such as iron or copper to the melt to precipitate sub-micron droplets of metallic copper. The glass from Tivoli shows characteristics of the latter group in terms of its very low lead, low copper and the sub-micron size of the colourant particles, but the colourant is predominantly cuprite. This is either because the conditions inside the glass passed into the cuprite field, after metallic copper had nucleated, or because the glass nucleated cuprite directly. Some metallic copper appears to have been originally present but we cannot confidently estimate the original proportion of copper particles because of problems with the decomposition of cuprite in the electron beam. However, it is likely that some of the subordinate metallic copper in this glass contributes to the colour.

The colour generation mechanism in early opaque red glass is thus complex. However, it appears that by the Roman period, the two distinct approaches, high-lead high-copper and low-lead low-copper, had become established and intermediate compositions were relatively uncommon (e.g. Freestone 1987). The analysis of the colourant phases has allowed us to appreciate the underlying technical reasons for these distinctive technological traditions.

The apparent ubiquity of halite particles in the glasses that we have so far studied leads us to question if this is a phenomenon limited to glasses which have been heat-treated, to promote the growth of colourant particles, or if it is a feature of all ancient glasses. If the former, it has potential as an indicator of heat-treatment. On the other hand, the occurrence of NaCl particles in all early soda-lime-silica glasses would be a potential source of error for analytical techniques that depend upon the production of a surface prepared using aqueous polishing media.

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Notes

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Chapter 12

The provenance of archaeological plant ash glasses

J. Henderson[1]

Abstract

There is very limited archaeological evidence for the primary production of plant ash glass in the Bronze Age and some evidence for its production in the Islamic period. It is therefore important to provenance such glasses in order to build up production and trade patterns. In this article archaeological, technological and scientific aspects of plant ash glasses are considered. Compositional characteristics of Bronze Age, Roman, Sasanian and Islamic glasses are considered in the context of being able to provenance them. There are promising signs that chemical analyses of some glasses provide an indication of their provenance, but it is not always easy to link compositional groups to production locations or production zones. However, isotope studies may provide an independent means of provenancing plant ash glass.

Introduction

The provenance of archaeological materials is important because it provides a means of assembling patterns of trade and interaction. Ultimately, a successful provenance can be attributed to a material if it has been produced using a geological material, or, in some circumstances (Weigand et al. 1977; Wilson and Pollard 2001), a material which has been manufactured using material of a geological origin. This kind of provenance allows one to link ancient products to the source of the raw materials used to make them. Materials such as turquoise (Weigand et al. 1977), limestone (Holmes and Harbottle 1994) and obsidian (Tykot 2002) have been used by man in their geologically unaltered state and, given the appropriate means of (chemically or isotopically) characterising them, offer a clear prospect of providing a provenance for artefacts made from them. The techniques that have been used to chemically characterise these materials have included optical emission spectrometry, neutron activation analysis, and laser-ablated inductively coupled plasma emission spectrometry. However, what archaeologists and archaeological scientists are often interested in is the question of *where* artefacts were manufactured (their *source*). Although concentrations of artefacts of the same type may imply that they were manufactured somewhere close to the concentration, an obvious way of proving it is archaeological evidence for the process of manufacture. The question then arises as to whether it is possible to characterise the materials used in the production process sufficiently as to be able to state that they are diagnostic to particular production sites and production phases. If the production site turns out to be close to the source of the raw materials used, this is a powerful combination of evidence in both archaeological and compositional terms.

Since the same or similar objects may be made on a number of different sites, it is important to be able to characterise the material sufficiently to be able to distinguish between the products of different production sites or zones. In addition, one should never underestimate the potential complexity of ancient production industries which can include the use of raw materials from a range of sources. The ease with which different raw materials can be transported to a production site can also play a part here.

In some cases materials such as obsidian or limestone from specific sources may have been used to make objects for well-defined periods. These periods will be dated at the site at which the objects are found. Examples are the Neolithic use of obsidian in the Middle East (Blackman 1984) and medieval

French limestone sculptures (Holmes and Harbottle 1994). Therefore, if the characterisation of the raw material can be achieved successfully – and it is in its 'as received' form, then the provenance of the material appears to be relatively straightforward, largely because the geological materials are only being cold-worked and not generally altered by high temperatures during the production process. In addition they can not be mixed or recycled, something which could potentially produce a blurring of any chemical characterisation.

However, when dealing with synthetic materials such as glass, one is dealing with a *combination* of raw materials, which may have been purified, and melted at high temperatures. There is also the potential for adding scrap material. Glass production can be divided into primary and secondary production processes: primary production involves the fusion of raw materials whereas secondary production involves the working of ready-made glass (such as glass blowing). Archaeological evidence for both kinds of processes can be found at the same site, although the processes may also be site specific. Even though it may be possible to characterise raw glass chemically from the all-important primary production sites, there is a question as to whether this characterisation is the same as providing a provenance for the glass made there, since essentially the same recipe could be used to make raw glass on more than one production site. Work by Freestone and co-workers (Freestone et al. 2000) has shown that trace elements in some natron glass from the Middle East allows a distinction to be drawn between compositional types; Nenna et al. (1997) have demonstrated that natron glass made at Wadi el-Natrun can be characterised by low levels of a major component, calcium oxide. In addition, strontium isotope ratios in natron glasses have shown a distinction between (e.g.) glass production in the Levant and Egypt (Freestone et al. 2003).

This paper will focus on plant ash glass instead. Whereas the compositional variations in the silica sources used appear to be mainly responsible for providing compositional distinctions between natron glasses made in different areas, it is the *compositional variations* found in plant ashes that provide the best potential for providing regional or more local compositional fingerprints for plant ash glasses. This might ultimately allow glass interaction zones of characteristic glass compositions to be assembled. Determination of $^{87}Sr/^{86}Sr$ isotope ratios in Islamic plant ash glasses has shown that it is possible to provenance plant ash glass from production centres which are geographically relatively closer together than is generally possible between production zones for natron glasses (Henderson et al. in press) and will help to refine glass interaction zones. Early work by Brill et al. (1973) had already demonstrated that the determination of lead isotope signatures in yellow glass opacified with lead antimonate has provided evidence for different production spheres for this opacifier in Mesopotamia and Egypt.

The chemical analysis of plant ash glasses has provided some evidence of regional traditions of production. In this article archaeological and scientific aspects of plant ash glass production are discussed. Case studies are used in order to assess the potential that plant ash glasses can be provenanced. Before doing this, however, some aspects of ancient glass technology must be outlined.

Glass technology

A range of raw materials can be used in the manufacture of ancient glasses. A number of publications describe a range of ancient glass compositions which result from differing combinations of raw materials (Brill 1999, Turner 1956; Sayre and Smith 1961, 1967; Henderson 2000, 2002; Freestone et al. 2000, 2002; Shortland 2000; Wedepohl 1997). Most ancient glasses can be defined as being either of natron or plant ash soda-lime-silica types, characterised by low MgO (LMG) or high MgO (HMG) respectively. Since this paper focuses on plant ash glasses, the principal compositions and associated inferred raw materials of relevance to plant ash glasses will be discussed here. Although only a relatively small number of compositional data are available for Bronze Age soda-lime-silica glasses (Brill 1999; Shortland 2000; Rehren 2001; Henderson 1998; Nicholson and Henderson 2000) a larger database of Islamic glasses is available (see below). The information we have shows that both ancient Egyptian and Mesopotamian, and Islamic glasses were usually made using a combination of plant ash and silica (crushed quartz pebbles or sand). Islamic examples of a more unusual combination, that of plant ash and sand, have come to light relatively recently (Freestone and Gorin-Rosen 1999: 114 and Henderson et al. 2004). Suitable halophytic plants for glass making belonging to the family *Chenopodiceae* grew and still grow on the fringes of deserts. Species belonging to this family include *Salsola kali*, *Salsola soda* and *Hammada scoparia* (Ashtor 1992: 494); plants belonging to the genus *Salicornia* could also have been used. Chemical analyses of these ashed plants show that they would have not only introduced the alkalies soda and potassium oxide, but can be the principal lime source in the glasses

made from them (Brill 1970; Barkoudah and Henderson 2006). The use of ground up quartz pebbles would have introduced silica and low levels of alumina, and may have been one source of iron impurities. Other silica sources such as quartz sand could have been used giving similar impurity levels.

The evidence for the primary production of both natron and plant ash glasses is provided by the existence of frit and raw glass attached to (tank) furnaces. Comprehensive evidence for tank furnaces has been reported by Gorin-Rosen (2000) from Bet Eli'ezer (Hadera) and Bet She'arim (Brill and Wosinski 1965; Freestone and Gorin-Rosen 1999) in the Levant and at Raqqa, Syria (Henderson 1999). Tank furnaces are thought to have functioned by the addition of the raw materials to the furnace in an appropriate ratio. However, given the relatively large volume occupied by plant ashes, fritting is a likely first step. Freestone has suggested that there might be compositional variation during successive melts from the use of such a furnace; the only way to show this is by excavation and analysis of furnace remnants where variations can be monitored '*in situ*' (Freestone 2002). Glass found attached to crucibles is more likely to be a result of glass-working.

In terms of the provenancing of plant ash glass, there is always a possibility that glass made elsewhere was added to the batch in the furnace in order to promote efficient fusion. However, if plant ash glass was made in massive quantities at the production site, it is more likely that locally made glass was added which would not change the chemical characteristics of the glass melt. If highly coloured lumps of glass were added as a secondary process to smaller quantities of raw (green) glass – in an Islamic production model – this might increase the possibility of introducing glass made using significantly different sources of silica or plant ash.

A compositional distinction between the *raw glass* known to be made in two production sites is self-evidently a means of distinguishing between them. Although there is quite a strong possibility that glass was fused at Tell el Amarna in Egypt (Nicholson and Henderson 2000), only one Bronze Age site (Rehren and Pusch 2005) has provided definite evidence for primary glass production, so provenance is still a problem for Bronze Age glass. Unless we have this crucial evidence we have to fall back on sites where glass working can be shown to have occurred, and glass making is inferred. Nevertheless, the identification of sites where secondary glass production has occurred, especially of basic pale green glass, may increase the possibility that primary glass production can be provenanced. This depends on the scale and organisation of glass production for the particular socio-economic and socio-political contexts in which it occurred.

Plant ash glasses were made at various times in the history of ancient glasses, starting from the earliest Bronze Age glasses in Mesopotamia and Egypt, including a few Roman examples, in the Middle East in the Sasanian period (2nd–6th centuries) and were fully reintroduced there during the Islamic period from about the early 9th century. Plant ash glasses were made in northern Italy, including Venice, from as early as the late 13th century using plant ashes imported from the Levant (Jacoby 1993). Given that these glasses, irrespective of their period of production, appear to have been made from a mixture of ground quartz and a plant ash, it is of interest here to compare some of the compositional characteristics of the plant ash glasses (PAGs) made at different times and in different places so as to investigate the potential for provenancing them.

A production model for Bronze Age glass in Mesopotamia suggested by Moorey (1994: 201–2) was for a specialised industry located in a restricted number of centres, within the orbit of major royal centres or temples. In the Bronze Age Mediterranean the highly controlled addition of very low levels of a cobalt-rich colorant to produce a blue colour in plant ash glasses led to the production and distribution of glass ingots (Nicholson et al. 1997; Henderson 2000: 60). For opaque yellow glass, lead isotope signatures appear to show two distinct production zones, in Mesopotamia and Egypt (Brill et al. 1973) – although this is not necessarily a reflection of where the raw glass was fused. Shortland (2002) has suggested, on the basis of LA-ICPMS analyses, that antimonate colorants were possibly derived from the Caucasus region. The scale of production in the other major period when plant ash glass was made, the Islamic period, was, by comparison, massive. Glass and other materials were often manufactured as part of a fully-developed urban landscape. For example, in northern Syria a 2 km long industrial complex has evidence for primary and secondary (glass-blowing) manufacture of glass in 8th–9th, 11th and 12th century phases, primary production occurring in tank furnaces (Henderson 1999). A model that has been suggested here is that when Raqqa was the capital of the 'Abbasid caliphate it acted as a major production centre – when the caliph moved to Baghdad (in 809) glass production continued at Raqqa, and it would also then have started in Baghdad. Raw materials would have been drawn from the local environment around Baghdad (Henderson 2003). Thus in contrast to Bronze Age

glass production, primary glass production in the Islamic world would probably have been more widespread and would have occurred on a massive scale.

Some possible reasons for compositional variation in plant ash glasses

Before we consider different plant ash glass compositions, the possible reasons for compositional variations in plant ashes must be considered. As Tite (2001) has noted, it is important to consider possible changes in the compositional 'fingerprint' of raw materials during the production of the finished artefact. If we take as a given that combination of quartz and plant ash form the basic recipe for the production of plant ash glass, there is a number of possible ways in which the chemical compositions of glasses could vary as a result.

Firstly, the source of silica must be considered. Progressive increases in the levels of alumina in plant ash glasses are thought to reflect the use of quartz, chert and sand respectively. Thus, on the assumption that alumina-bearing minerals such as feldspars are the primary source of alumina, 'typical' plant ash glasses (PAGs) will contain around 1% alumina, the inference being that quartz has been used. Conversely, alumina levels of 2.5–3.0% or higher are thought to reflect the manufacture of a more unusual kind of plant ash glass, made from sand. The publication of the chemical composition of ashed '*Keli*' (Turner 1956) and '*Keli*', *Salsola* and *Salicornia* (Brill 1970, Table 2) and others (Barkoudah and Henderson 2006) suggests that the plant ashes are unlikely to contribute significantly to the alumina levels found in PAGs.

Ashed plants can potentially introduce soda, potassium oxide, magnesia, sulphur trioxide, chlorine, phosphorus pentoxide and iron oxide. There is a far wider series of factors which could potentially cause compositional variations in the glasses made from them and which could therefore, in combination, potentially provide a means of provenancing the glasses. These include the use of different plant genera (such as *Salicornia*, *Salsola* and *Hammada*) and the geological conditions in which the plants grow (Barkoudah and Henderson 2006). Shrubby halophytic plants would be collected and burnt in their entirety. A further complicating factor could be that ash compositions change with temperature. Further parameters which could potentially affect the compositions of plant ash glasses would be mixing of plant species or silica sources. It is, however, unlikely that plants growing in different geological conditions would be mixed given that the plants would probably have been selected from the same area. As already mentioned, large quantities of Islamic raw plant ash glass were melted in a single stage by combining quartz and plant ash in tank furnaces. The possibility that the raw materials were fritted can not be ruled out. It is debatable, however, whether fritting would have changed the chemical composition of the final raw glass: it would however have reduced the number of gas bubbles and allowed a better fusion of raw materials. On the other hand the tank furnaces at Raqqa achieved a minimum temperature of 1250°C. (McLoughlin 2003) so the fusion of raw materials and evolution of bubbles would have been effective. Finally, the mixing of raw glasses of different compositions may have occurred; where different PAGs made with sand and quartz were mixed we would expect to find a mixing line for all contents. This inference has been drawn from glasses analysed from the factory site of Raqqa, Syria. Here, three distinct compositional types of PAGs have been identified (labelled 1, 2 and 4 – the fourth glass being a natron glass), and there is no compositional evidence of mixing between the two largest plant ash glass groups, types 1 and 4 (Henderson et al. 2004).

The chemical compositions of PAGs are the net result of these potential variations. The question remains as to whether the combined result of using a range of technological procedures to make the PAGs would create a distinctive chemical composition characteristic to the time and/or place of production (Rehren 2008). It is clearly important for the question of glass provenance and it is this aspect which will be considered next.

Case studies

The following examples have been selected so as to reflect different production systems which would have been dependant on differing socio-economic and socio-political contexts. Whilst it is clear that trace element levels in ancient glasses have a potential to contribute to their provenance and to distinguish between those produced at different production centres (Freestone et al. 2000: 73, Fig. 9; Shortland 2002), the discussion here will focus instead specifically on examples of major components (CaO and Na_2O) and minor impurities (Al_2O_3 and MgO) in PAGs. As noted above, Na_2O, MgO and CaO are thought to have been introduced in the plant ash and Al_2O_3 in the silica source. Data sets of PAGs will be used from a broad chronological spectrum so as to highlight the potential and limitations of such an approach to provenance. The glasses to be considered will be those from 14th century BC Bronze Age Tell

Brak, Syria (Brill and Shirahata 1998; Henderson 1998), 14th century BC 18th Dynasty Tell el Amarna, Egypt (Brill 1999, Table I A), 1st century AD Roman Fishbourne, UK (Henderson 1996), 4th–5th century Sasanian Ctesiphon, Iraq (Brill 1999, Table VI D), 9th–11th century Islamic Raqqa, Syria (Henderson et al. 2004), 11th century Islamic Banias, Israel (Freestone et al. 2000, Table 2) and the 11th century 'Islamic' Serçe Limani shipwreck (Brill 1999, Table VII I). The large number of compositional data for Islamic glasses will be dealt with in most detail, including the potential for provenancing the glasses concerned. Of the periods considered, it is only in this period that it is possible to draw on large data sets of *raw* plant ash glasses; interpretation of data from the other periods is therefore somewhat limited, being based on secondary products for which we are unable to suggest specific production centres with the same confidence.

A comparison between relative Al_2O_3 and MgO levels in contemporary glasses from 14th century non-cobalt blue Tell Brak and Tell el Amarna (Fig. 1) reveals that glasses from both sites have been made from a relatively pure source of silica with respect to the Al_2O_3 levels. Most Amarna data forms a relatively tight cluster, especially with respect to MgO, which suggests a restricted range of variation in the use/preparation of plant ash. Brak glasses on the other hand fall mainly on both sides of the Amarna data with a much wider scatter of values, possibly indicating the use of a wider range of plant species and/or reflecting wider variations in geology. The relative levels of soda on the other hand are generally higher in Amarna glasses (Fig. 2). The data published by Brill and Shirahata and by the author both reveal a range of soda levels for Brak glasses with (for the electron microprobe analyses) high analysis totals; low soda levels can *not* therefore be attributed to weathering and represent a real technological difference between the Amarna and Brak glass. In addition, it further underlines the wider variation in the plant ash compositions used for the manufacture of the Brak glass.

The plant ash glass data for Ctesiphon and the

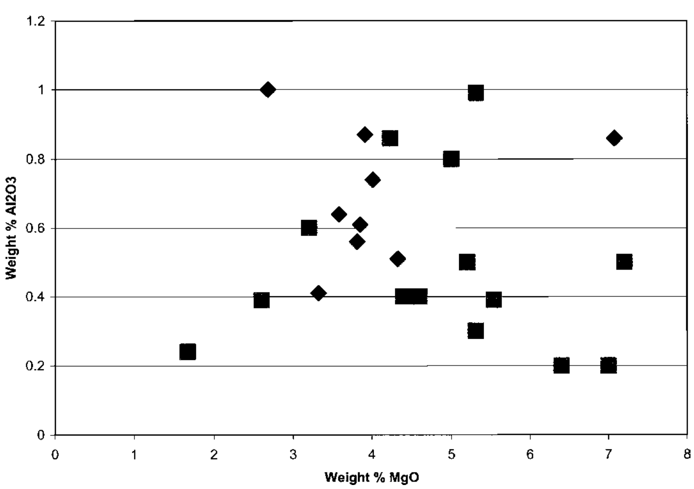

Figure 1: A comparison between relative Al_2O_3 and MgO levels in contemporary non-cobalt blue glasses from 14th century Tell Brak (■) and Tell el Amarna (♦).

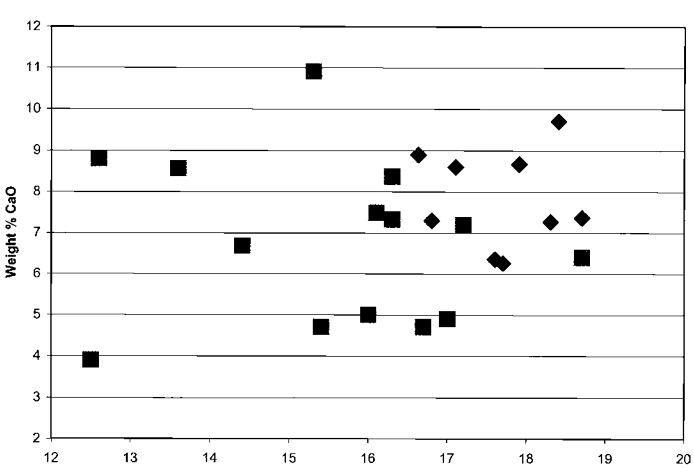

Figure 2: A comparison between relative Na_2O and CaO levels in contemporary non-cobalt blue glasses from 14th century Tell Brak (■) and Tell el Amarna (♦).

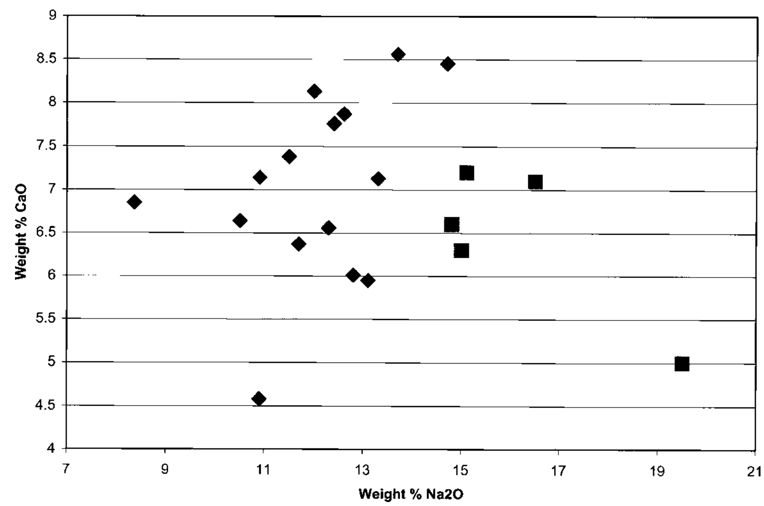

Figure 3: A comparison between relative Na_2O and CaO levels for Ctesiphon (♦) and the unusual plant ash Roman glasses from Fishbourne (■).

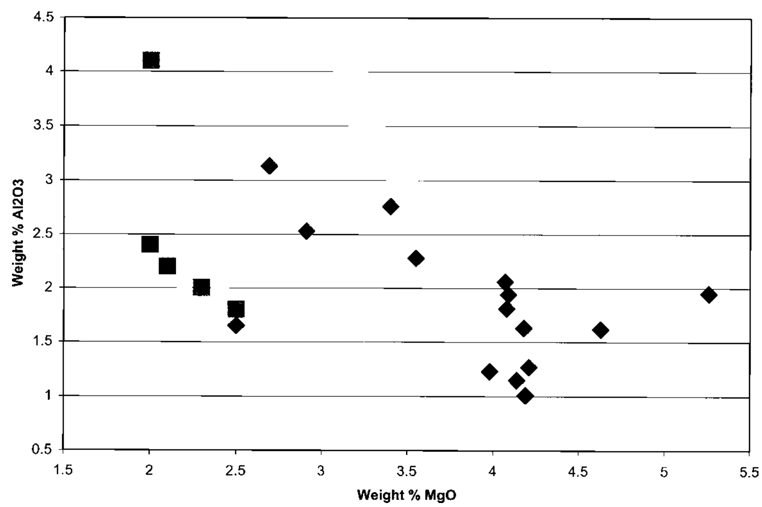

Figure 4: A comparison between relative Al_2O_3 and MgO levels for Ctesiphon (♦) and the unusual plant ash Roman glasses from Fishbourne (■).

unusual plant ash Roman glasses from Fishbourne do however exhibit a distinction according to their relative soda levels, with the Roman glasses containing distinctly higher levels (Fig. 3). The Fishbourne glasses contain relatively low MgO levels, and four sit on a negatively correlated dilution line (Fig. 4) which might suggest mixing with the far more common natron glass and which helps to explain the relatively low magnesia levels in the Fishbourne glass.

In the Islamic period we have the luxury of being able to consider the chemical analyses of raw glass. Here (Fig. 5) the relative levels of MgO and Al_2O_3 in contemporary raw glass from Banias and Serçe Limani provides a means of distinguishing between them. Neither of these collections of raw glass were derived directly from factory sites and are likely to represent glass made during single phases of production rather than a mixture of the products of separate melts from a factory site over a period. This latter scenario is a probable explanation for the scatter of points from raw glass found attached to tank furnace fragments at Raqqa, Syria. The range falls into the three main PAG compositions identified from Raqqa (Henderson et al. 2004), one of which is similar to the Serçe Limani raw glass. Otherwise the raw glass from the three sites is compositionally distinct. The relative dispersion of the Islamic PAG data is therefore a reflection of the archaeological context in which they have been found. These clusters of raw plant ash glass data provide a base line for the provenancing of factory plant ash glasses. Often it is likely to be more a case of being able to state that a glass was *not* made at (e.g.) Raqqa rather than being able to say, necessarily, that it definitely was. This is always likely to be the case because it is most unlikely that we will eventually find a full range of Islamic glass factories which represent the full range of recipes for raw plant ash glass. A plot of weight % CaO vs. weight % Na_2O for these glasses (not included here) reveals that most are calcareous, containing above 8% CaO, with some raw Raqqa glasses containing lower levels of CaO.

If we add MgO and Al_2O_3 data for vessel glasses

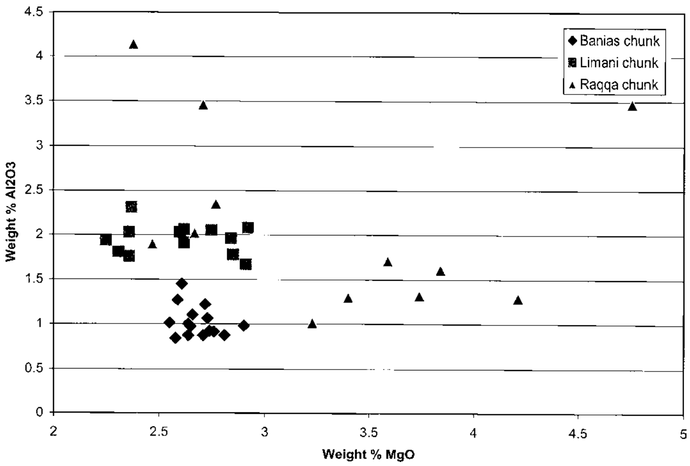

Figure 5: A comparison between relative Al_2O_3 and MgO levels for contemporary raw glass from Banias, Serçe Limani and Raqqa.

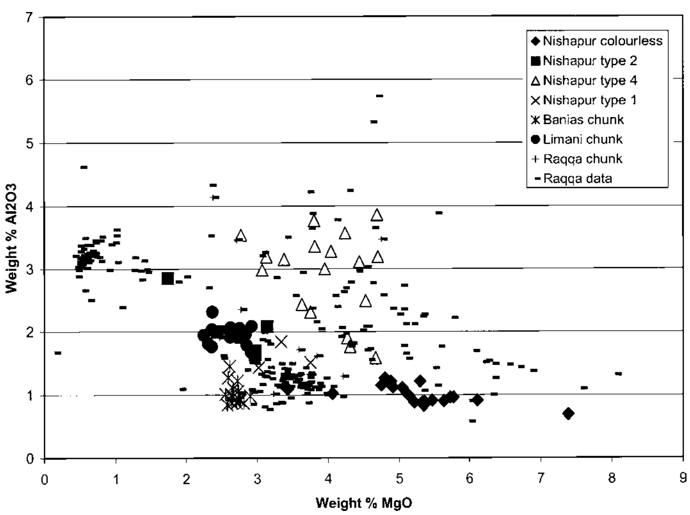

Figure 6: A comparison between relative Al_2O_3 and MgO levels from Figure 5 plus data for vessel glasses from 9th century Nishapur and 8th–11th century Raqqa.

from 9th century Nishapur and 8th–11th century Raqqa, a number of features are apparent (Fig. 6). Firstly, most colourless Nishapur glass can be seen to cluster tightly which suggests that, like the Banias and Limani raw glass, they are the result of a technology with tightly defined procedures. Secondly this colourless glass was apparently not made at the centres which produced the raw glass found at Banias, Limani and Raqqa. It may therefore represent a separate Islamic PAG production zone probably in Iran – and this is also borne out by the CaO versions Na_2O plot (Fig. 7). In addition, although Nishapur 'type 4' glass is of a Raqqa type as defined by relative Al_2O_3 and MgO levels, it can nevertheless be distinguished by higher soda levels (Fig. 7).

This indicates that although similar levels of MgO and Al_2O_3 have been introduced into the Raqqa and Nishapur melts, the higher soda levels (Henderson 2003, Table 2, Figure 8) may suggest that a slightly different plant species or sub-species has been used to make it. On the assumption that the Nishapur glass was made in Iran, these results therefore appear to provide a tentative means of provenancing the Nishapur colourless and 'type 4' glasses. Nishapur type 2 glasses appear to correlate with chunk glass from Limani, but can also be distinguished by their higher CaO levels, again suggesting the use of a slightly different kind of plant ash. When compared to contemporary Raqqa glasses, Nishapur colourless glasses are quite distinct: type 2 Nishapur glasses contain a mean of 7.4% CaO, whereas Raqqa type 2 glasses contain a mean of 5.39% CaO (Henderson 2003, Table 2). The type 4 Nishapur and Raqqa glasses characterised by medium levels of Al_2O_3 can be distinguished by their soda levels, Nishapur containing a mean of 16.7% whereas Raqqa contains a mean of 13.77% (Henderson 2003, Table 2). These differences therefore underline the distinctiveness of the Iranian glasses and reflect the historical and archaeological evidence for northern Iran being a key production centre in the 9th–10th centuries.

Taking all of the Al_2O_3 and MgO PAG data together

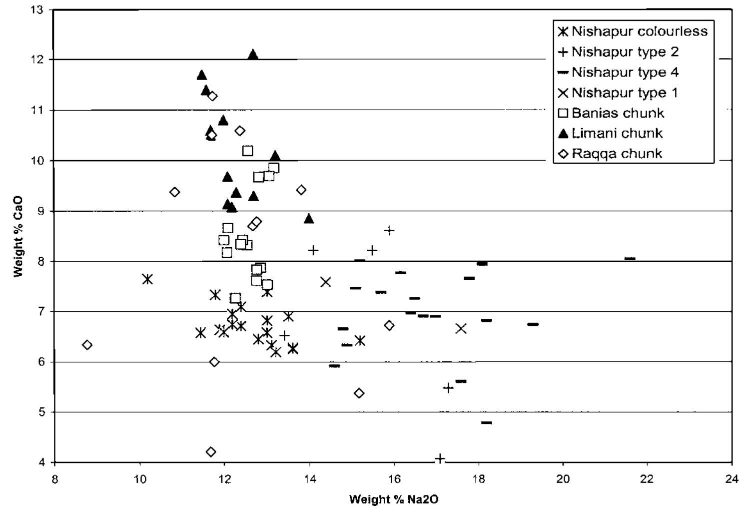

Figure 7: A comparison between relative CaO and Na_2O levels for glasses from Banias (chunk glass), Serçe Limani (chunk glass) Raqqa (chunk glass) and Nishapour.

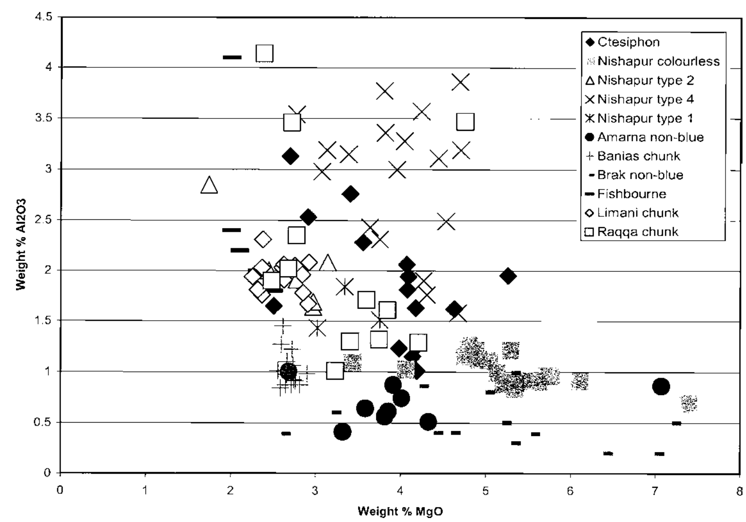

Figure 8: A comparison of Al_2O_3 and MgO PAG data together for all periods.

for all periods (Fig. 8), it is clear that 14th century BC Brak and Amarna glasses contain the lowest Al_2O_3 levels, suggesting that the purest source of silica was used to make them. The colourless Nishapur vessel glass samples and the Banias raw glass also contain relatively low Al_2O_3 levels, but these levels are in line with some raw plant ash glass that has been found at Raqqa. This figure underlines the distinctiveness of Nishapur 'type 4' glass.

Discussion and conclusions

There is little question that in order to understand the archaeological context of glass production it is important to discover more primary and secondary glass production sites. It is also important to attempt to establish any links between vessel form and chemical composition. Firstly, this may reveal links between glass working properties determined by chemical compositions and the extent to which glass workers used those properties deliberately. Secondly, regional specialisations in vessel form/decoration may be revealed.

The chemical compositions of ancient plant ash glasses can be quite variable, depending on the plant species used to make them, the geological environment in which they grew and the ways in which the plants were prepared for glass production. These factors will determine variations in glass chemical compositions to a greater or lesser extent depending on the scale and context (political, social, economic, ethnic) in which the glass was made. It is, nevertheless, possible to associate particular compositional types of plant ash glasses with specific production sites or zones. The challenge comes in being able to state categorically that the combination of raw materials used to make the glasses on those sites were not repeated elsewhere, leading to similar chemical compositions and to overlapping compositional 'groups'.

Certainly analyses of the raw glasses found at the factory site of Raqqa demonstrate the possible range

of plant ash compositions that could be melted at one site; the analyses of collections of raw glass from two other sites, Banias and the Serçe Limani shipwreck, indicate that they were probably the result of single melts from respective production sites and that they are compositionally distinct. In addition it has been demonstrated here that some Islamic plant ash glass vessels from Nishapur in Iran are compositionally distinct from those melted in Raqqa and from the raw plant ash glass found at Serçe Limani and Banias. This is therefore quite promising for the provenance of Islamic plant ash glasses.

Moreover, by determining the isotopic signatures of (halophytic) plants growing near production sites such as al-Raqqa and comparing them to the raw glass found on such a site, it has become possible to build up a local signature for the plants and the glass made from them, because $^{87}Sr/^{86}Sr$ isotope ratios found in plants are a reflection of the bedrock geology on which they grow (Sillen et al. 1998; Evans and Tatham 2005). On this basis it has been demonstrated that plant ash glass from Banias and Raqqa can be distinguished, providing a firm provenance for the glasses (Henderson et al. 2005). For the technique to be successful as a provenancing tool it relies on a minimum amount of glass mixing – especially the addition of plant ash glasses made in other geologically contrasting areas with different Sr isotope signatures. However, the import of halophytic plants or plant ashes into areas where they grow commonly is very unlikely. Given that plant ash glass is relatively easy to make, the possibility of adding 'foreign' glass made in a different geological zone to a primary glass melt is likely to be minimal. Strontium isotope determinations overcome the potential compositional variations in the glasses which might be caused by mixing plants of different species or variations in the technique used to prepare the plants; the same isotopic signatures will be obtained irrespective of the species as long as they are growing in an area dominated by bedrock of the same age. Moreover, because different Sr budgets are involved in the production of plant ash and natron glasses, the strontium ratios in these two glass types confirm the raw materials inferred from their chemical compositions (Freestone et al. 2003; Henderson et al. 2005). Because of these differences it should be possible to show when plant ash and natron glasses have been mixed, producing a clear mixing line.

There is no particular reason why groupings of glass chemical compositions should necessarily be the same as those produced by isotopic signatures: isotopic signatures are a reflection of the geological age of the raw materials used and can provide locational/ environmental information. Contrasts in the chemical composition of glasses relate to variations in the chemical compositions of the raw materials used and do not *necessarily* provide independent locational information. However, when the two agree, they provide a firm proof of provenance, as for Banias and Raqqa glasses. Plant ash glasses with indistinguishable chemical compositions made at two different locations could be distinguished using strontium isotope ratios. Another possibility is that two compositional groups of plant ash glasses can be identified, but that strontium isotopes reveal the use of plants being isotopically indistinguishable. This also adds to the information regarding the glass production technology. With the determination of sufficient isotope signatures for raw plant ash glasses from production sites and isotopic signatures of glass vessel fragments it should become possible to provenance the vessels. Overall, it is clearly time to re-evaluate the assertion that 'it is not surprising that glass has been the least successful ancient material to be studied from the provenance perspective' (Wilson and Pollard 2001: 512).

Notes

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2 After this article was completed two articles on Bronze Age plant ash glass compositions have been published which have increased significantly the number of compositional data (Nikita and Henderson 2006; Shortland and Eremin 2006).

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Chapter 13

Microanalysis of glass by Laser Induced Plasma Spectroscopy

M.S. Walton[1]

Abstract

The goal of this preliminary work was to achieve spatially resolved chemical analyses using laser induced plasma spectroscopy. A Q-switched Nd:YAG laser operating at its fundamental wavelength of 1064 nm was tightly focused onto samples mounted to an x-y translation stage of a polarizing light microscope. The radiation from the focused laser generated a spark at the sample surface vaporizing material into a short-lived plasma plume. An optic fiber positioned as close as possible to the plume captured the plasma emission and channeled it to a miniature Czerny-Turner spectrometer with a spectral range from 200–850 nm and 1.3 nm resolution. Imaging and targeting of the laser onto sample features was performed through the optical path of the light microscope. With the present setup, spot sizes of 25–30 μm were realized at laser energies of 75 mJ pulse^{-1}. The performance of the laser microprobe was evaluated through the analysis of several elemental oxides and standard glasses.

Introduction

Due to the inherent complexity of vitreous materials, the archaeometric attempts to establish the fabrication technology of glasses and glazes from the ancient world have proved challenging and at times contentious (e.g., Rehren 2003; Mass et al. 2002; Shortland and Tite 2000). Consequently, analysis of these materials demands the quantitative precision generally offered by electron probe microanalysis (EPMA) or mass-spectrometric techniques. However, due to the expense of such equipment and their lack of portability, these elemental analysis techniques are not always cost-effective for museum laboratories, nor practical for use in the field. This current work explores the use of a laser induced plasma spectrometer (LIPS) as a cheaper and potentially field worthy instrument that can meet the rigor expected of the analysis of archaeological material.

LIPS is based upon the detection of atomic emissions in a hot plasma (T = 10,000–20,000°K). The plasma is produced by a high intensity laser source incident on a surface that causes ejection and vaporization of material. Because the plasma can be localized to a discrete area around 10–30 μm in circumference, surface damage may be minimized often with material loss on the order of 1 ng to less than a μg. As a result, this technique can be considered to be micro-destructive and appropriate for many conservation and archaeological applications.

Laser induced plasma spectroscopy is not a new technique. The first commercial LIPS instruments were built in the late 1960's, but were relegated to the status of experimental novelty until very recently (Moenke-Blankenburg 1989; Radziemski and Cremers 1989). The current progress in LIPS microanalysis has been fueled in part by advances in lasers, fiber optics, and gated CCD detectors. However, the technique has become popular primarily due to the ever-increasing need for rapid in-situ analyses required in harsh environments (i.e., Mars and other toxic locals) and industrial online processing (Fink et al. 2002; Hubble et al. 2002). LIPS has proven to be particularly effective in these circumstances because of its ability to determine the full suite of major and trace elements

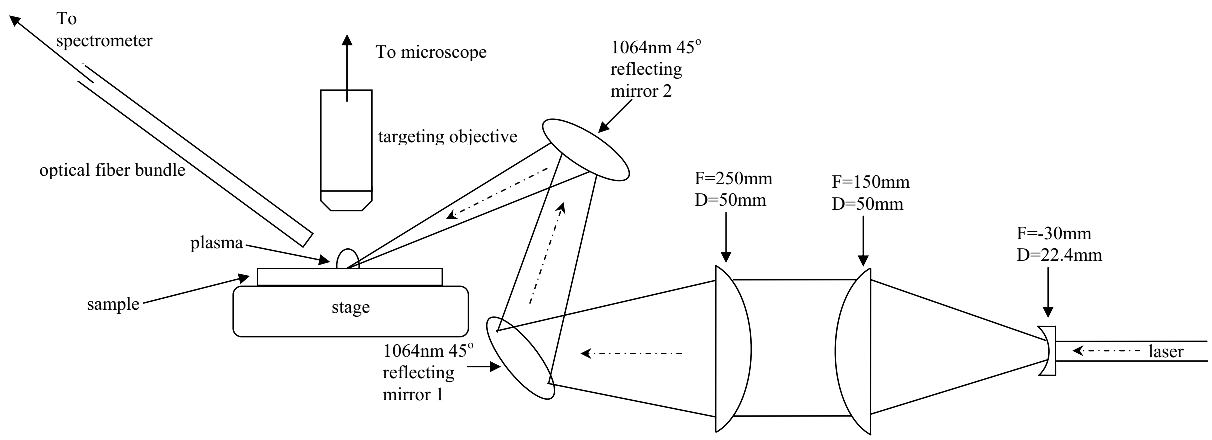

Figure 1: Optical path layout and detection setup of the Laser Induced Plasma Spectrometer.

in a material in a matter of seconds with the added benefit of requiring little or no sample preparation.

In the fields of archaeology and conservation, LIPS still remains on the periphery of analytical techniques routinely employed. Although several technical notes have highlighted its potential applications, no study as of yet has been conducted (to the knowledge of the Author) which utilizes the technique in any in-depth examinations of archaeological material (Müller and Stege 2003; Angolos et al. 2002; Angolos et al. 1997). While the work presented here does not go any further than others in addressing this issue, the intention of the LIPS instrument being developed at Los Angeles County Museum of Art is for it to eventually replace the aging electron microprobe facilities.

Experimental

All of the LIPS experiments were performed in air at ambient temperature and pressure. The apparatus consisted of a 3.5 ns pulse-width Q-switched Nd:YAG laser (Infinity, Coherent, Santa Clara, CA) focused through a series of lenses onto the stage of a light microscope (Universal, Carl Zeiss, Germany). The laser was operated at its fundamental wavelength (λ=1064 nm) one shot at a time with energy attenuated to 75 mJ pulse^{-1} as was measured by a power meter (LaserMate-P, Coherent, Santa Clara, CA) placed in the beam path. Light emitted from the plasma was collected by an optical fiber bundle connected to a Czerny-Turner spectrometer with a 2048–pixel linear array CCD detector (S-2000, Ocean Optics, Dunedin, FL). The spectrometer has a 200–850 nm range with 600 mm^{-1} grating and a 25 μm slit. This allowed for a nominal spectral resolution of 1.3 nm. Imaging and targeting of the beam on the sample was performed by the light microscope.

The optical train and layout of the experimental setup can be seen in Figure 1. The collimated beam was demagnified through a telescopic arrangement of lenses with final focusing done through a long focus (F=250 mm) lens (all optical components, Edmund Industrial Optics, Barrington, NJ). After exiting the final lens, the beam was folded through a Z-shaped arrangement of mirrors with the intention of creating a low aspect ratio beam waist when it was finally delivered to the sample. With this arrangement, a final beam spot size of 30 μm was achieved at the sample surface. The plasma emission was collected by fiber optics at an approximately 45° angle to the direction of the laser propagation and plasma spark. The design of this arrangement is an adaptation of the apparatus used by Radivojevic et al. (2004). Its primary function was to separate the optical path of the beam from that of the microscope. Other researchers have used light microscope optical paths to successfully focus laser light to small spot sizes, but this is at the cost of small working distances (~1 mm) between the objective and sample (Gornushkin et al. 1999). Such short distances become problematic with regard to contamination and damage of the microscope objective by the ablation plasma. Also, this makes observation of the plasma by fiber optics difficult because of the low solid angles available for imaging.

To reduce detection of the initially intense blackbody radiation generated from the plasma, the spectro-

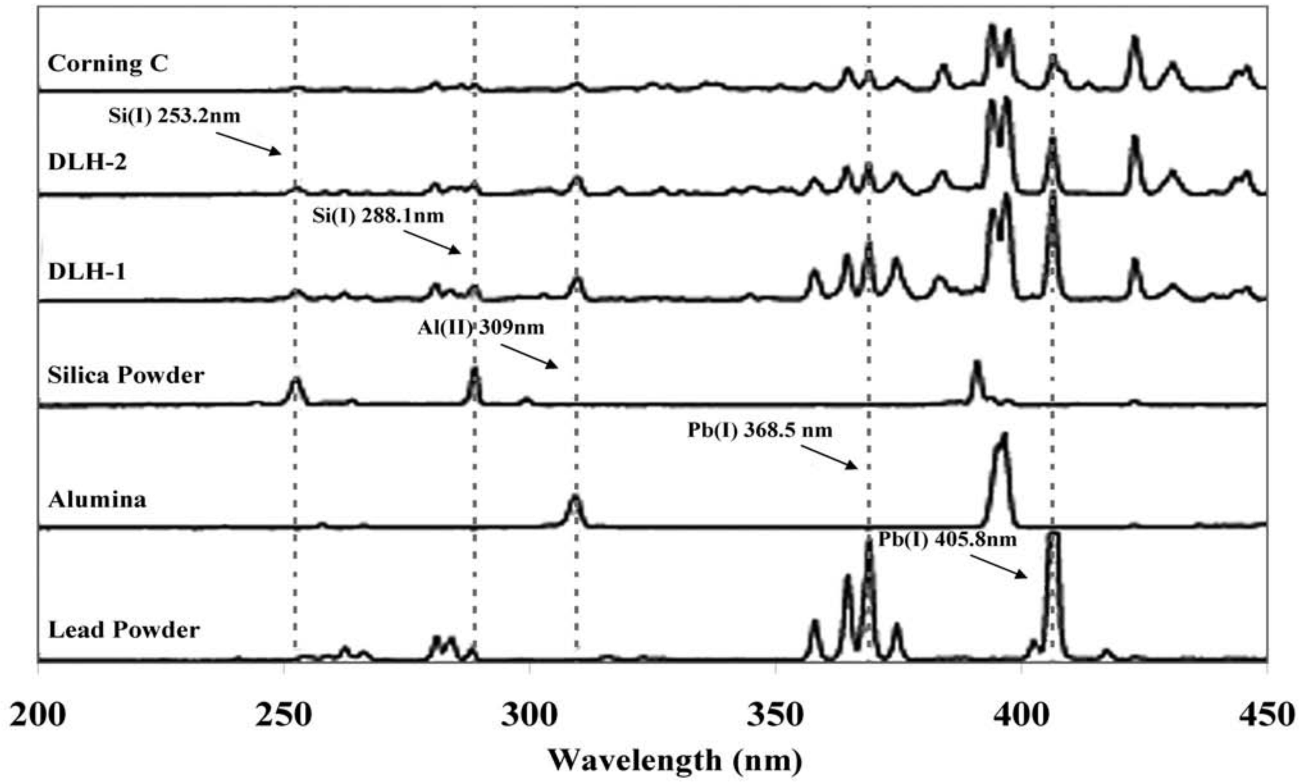

Figure 2: LIPS spectra of lead silicate glasses and elemental powder standards in the VUV-UV range. Marked peaks show some of the bands used in quantification of these standards.

meter was time-gated through a high precision delay trigger native to the Infinity laser hardware. On arrival of the laser shot, a 10 μm delayed TTL pulse was sent from the laser thereby triggering the spectrometer which integrated the received emission signal over 27 ms.

A series of different composition glasses was analyzed to assess the initial performance of the instrument. These included two soda-lime silicate standard glasses (Corning-A and Corning-C, Corning Glass, Corning, NY), two lead aluminosilicate glasses (DLH-1 and DLH-2, in-house standards produced for RLAHA, Oxford, UK), and one potassium based glass (Corning-D, Corning Glass, Corning, NY). Along with these glasses, several pure powder standards (Al_2O_3, PbO, and SiO_2, Loch-Light Laboratories, Colnbrook, England) were compacted into disks using a hydraulic press prior to analysis.

For each sample, six spectra were collected and averaged together. To these average emission spectra, a cubic polynomial baseline was least squared fit to subtract continuum. Emission bands were then identified and fit with Gausses to retrieve peak amplitude and area. For calibration plots, the background under each band was integrated as a reference signal and used for normalization (Cáceres et al. 2001).

Results and Discussion

Selected LIPS spectra are shown in Figure 2. The region covered in this figure belongs to the visible ultraviolet through ultraviolet where many of the useful emission lines may be observed. The bands marked in this plot correspond to the three most abundant elements in the lead silicate glasses examined: Si, Al, and Pb. Also shown are spectra of the corresponding pure oxides of these elements. These LIPS data clearly demonstrate that the qualitative assessment of composition in these glasses is relatively simple.

Further attempts at developing a quantification routine were also explored. Figure 3 shows the calibration curves for Na and Ca inclusive of each of the glasses analyzed. These curves demonstrate a good linearity within experimental error and were therefore deemed suitable for calibration. However,

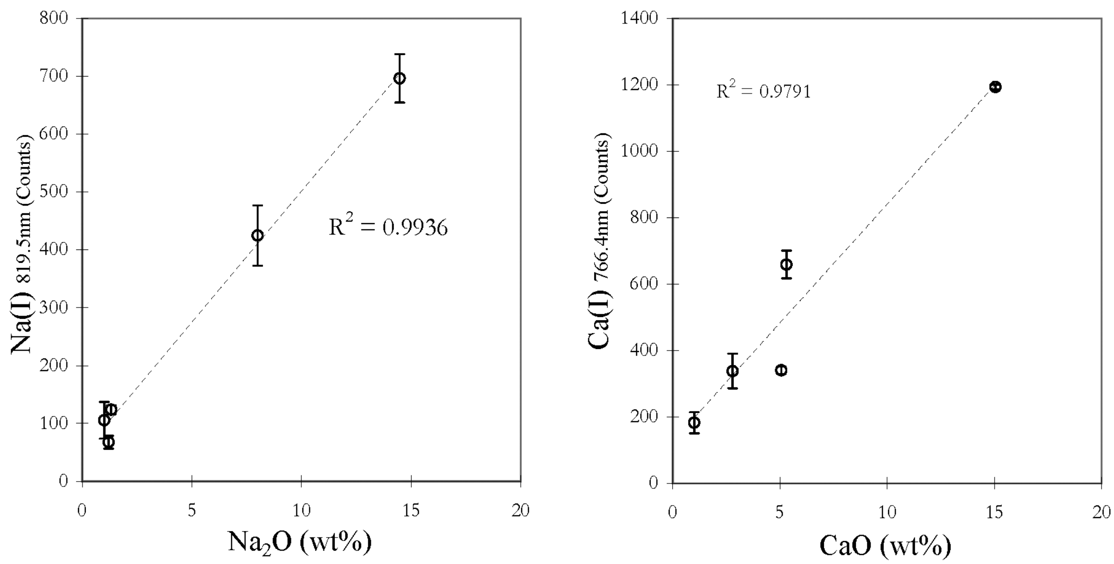

Figure 3: Calibration curves for Na_2O and CaO in standard glasses. Intensities of the Na (I) band at 818.4 nm and Ca (I) at 422.7 nm were normalized by the integrated continuum intensity under the bands (I_{Ref}).

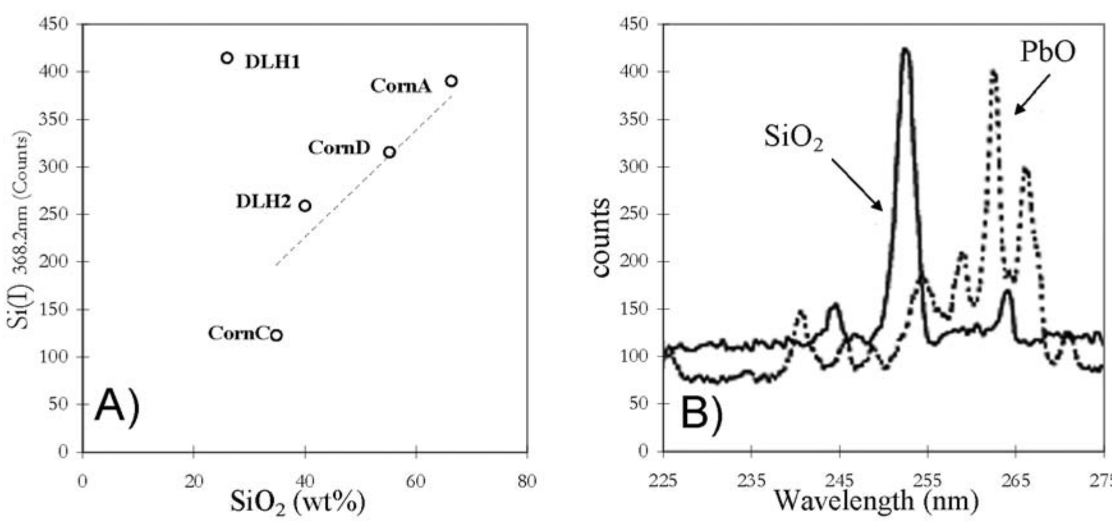

Figure 4: A) Calibration curve for SiO_2. B) Section of spectra taken in the VUV of SiO_2 and PbO powders showing overlap between the measured SiO_2 band and some of the secondary Pb bands.

as may be seen in Figure 4a which shows the plot for Si, the quality of the calibration is poor due to the anomalous Si intensity observed in the DLH1 glass. Considering that DLH1 contains considerably more lead than any of the other glasses (66 weight %), this intensity was probably caused by severe peak overlap between the main Si band and secondary Pb bands. These peak overlaps may be observed in Figure 4b which shows the spectra for Si and Pb elemental oxides. If the measured DLH1 intensity is removed from the linear regression calculation, it may be seen that the curve shows a reasonable correlation between the measured and expected amounts of SiO_2 for the other samples. Band overlaps, such as those found here, can be removed with simple modifications of the experimental setup such as using a higher resolution spectrograph grating or by conducting the analyses in a buffer gas such as argon or nitrogen.

Conclusion

The LIPS setup at the Los Angeles County Museum of Art has been described. It was found that the qualitative assessment of both soda lime silicate glasses and lead silicate glasses was easily accomplished with this technique. It was also shown that quantitative analyses were achievable. With fine-tuning of the technique, LIPS promises to be a sound and cost-effective method for analyzing a wide array of archaeological and conservation materials.

Acknowledgment

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Note

1 Getty Conservation Institute, Los Angeles, California, USA.

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Chapter 14

New thoughts on niello

P. Northover[1] and S. La Niece[2]

Abstract

The detailed examination in cross-section of niello inlays from bronze, brass, silver and gold metalwork of different periods gives insights into manufacturing methods and workshop practices. Inlay techniques were adapted to suit the properties of the different metal sulphide recipes. The sources of niello, in particular the question of the secondary use of sulphide by-products from metal smelting and purifying was considered, but the manufacture of the sulphides in the workshop where the object was being made appears to be the usual practice.

Introduction

In his own research, and in his direction of others', Michael Tite has always looked beyond the simple compositional analysis of ancient artefacts to the underlying structure and material properties, and the processes that produced them. Over two decades ago he supported one of us (La Niece 1983) in a programme of research on the development and evolution of niello. The research used the analysis of niello on artefacts from the first century AD through to modern times to track the changes in technology in Europe and the Islamic world. The results established that, as a general rule, Roman niello is composed of the sulphide of one metal only, either silver or copper and, furthermore, the niello is usually made of the same metal as that of the object into which it was inlaid. This niello could not survive melting easily so was applied as a warm paste. Sulphides made with silver and copper together were introduced at the end of the fifth century, though silver sulphides were still being used for inlay. Lead was added to the ingredients as early as the eleventh century AD in eastern Europe. This composition will flow well when melted and therefore can be used to fill more complex designs. Both the structure and the material properties of the different sulphide recipes allowed conclusions to be drawn about the inlay methods but during this survey a few nielli were found which were inhomogeneous and not fully understood, using the methods of examination available at the time. Since then the capabilities of scanning electron microscopy and microanalysis have been greatly enhanced, thereby giving us the opportunity of increasing our understanding of how niello was made, how it was applied and how it degrades with time and the environment. In doing this we can look not only at the niello itself, but at detritus picked up on the workbench, and at the overall quality of manufacture. At the same time new archaeological and historical discoveries have provided us with samples which illustrate these processes very well. We therefore are pleased to offer these new results to Michael.

Niello is a black inlay material, made of metal sulphides, which is rarely used by European silversmiths and jewellers today, perhaps because of practical difficulties in achieving a good finish when compared to alternative materials such as enamel. In spite of this, it does have a very long history as a silversmith's technique, going back to at least the 4th century BC (Giumlia-Mair and La Niece 1998; La Niece 1998), though it did not become common until 1st century AD Imperial Rome. The Romans used it

Figure 1: Bronze jug (a), patera (b) and detail of niello decoration (c), from a Roman cemetery, Stansted airport.

extensively, especially to decorate silver table wares and gold and silver jewellery, often with gilding for a polychrome effect. The original research project (La Niece 1983) was carried out using X-ray powder diffraction analysis and energy dispersive X-ray analysis in an SEM. These methods were ideal for characterising metal sulphides, but it became clear that some of the inlays were not simple homogeneous mixtures of sulphides. In this study we have looked again at some of these complex mixtures and what they reveal about niello manufacture and inlay techniques. The question of sulphide by-products from metal smelting and purifying having a secondary use as niello was also considered.

Roman copper sulphide niello

The excavation of the Duck End Car Park site at Stansted Airport in the late 1980s revealed a rich Roman cemetery with some important bronze and brass vessels (Northover et al. 1991). One of the graves in this cemetery (Cremation 25) yielded two leaded bronze vessels inlaid with niello: a trefoil jug and a patera (Figure 1a-b). The body of the jug is made from two sections, both cast in leaded bronze. The lower part with its simple ribbed decoration has been finished on a lathe; the upper section clips into this with a simple mechanical joint with a flange on the upper section fitting inside a lip on the lower (Mutz 1972). The Medusa head handle is attached with a lead-tin solder. It is only the upper section that is inlaid, the inlay being in the forms of trefoils and palmettes. The patera has a cast body with a separate handle soldered in place. The bowl of the patera has also been finished on the lathe; it is ornamented with a niello-inlaid umbo (Figure 1c) soldered in place in the centre. The compositions of the bronze and niello in the patera and jug are presented in Table 1. All analyses are by electron probe microanalysis with wavelength dispersive spectrometry and they will be published in detail in the forthcoming excavation report.

The 1983 study showed that the Romans in the first century AD used plain copper sulphide for their niello when inlaying copper alloys. When polished this would tend to give a deeper and blacker gloss than silver sulphide. The vessels from Cremation 25

Table 1: Analysis of inlaid Roman bronzes from Cremation 25, Duck End Car Park, Stansted Airport (wt%).

Sample	Object	Part	Fe	Co	Ni	Cu	Zn	As	Sb	Sn	Ag	Bi	Pb	Au	S
DCS1	Patera, handle	umbo	0.63	0.01	0.02	79.09	0.45	0.20	0.06	10.25	0.05	0.01	9.16	0.00	0.04
DCS2	Patera, handle	handle	0.78	0.01	0.03	84.40	1.30	0.24	0.12	10.42	0.01	2.00	1.78	0.03	0.02
DCS3	Patera, handle	body	0.42	0.01	0.03	69.66	0.35	0.11	0.12	15.06	0.08	0.00	14.09	0.03	0.05
DCS37	Patera, handle	niello	0.05	0.00	0.01	81.76	0.06	0.29	0.02	0.56	0.02	0.00	0.00	0.00	17.21
DCS6	Jug, handle	base	0.01	0.00	0.02	76.17	0.01	0.02	0.10	13.67	0.04	0.01	9.89	0.00	0.05
DCS7	Jug, handle	rim	0.01	0.01	0.03	74.51	0.03	0.22	0.12	12.82	0.05	0.01	12.24	0.00	0.06
DCS8	Jug, handle	patch	0.03	0.01	0.02	70.85	0.06	0.16	0.11	15.97	0.05	0.01	11.25	0.04	0.05
DCS9	Jug, handle	handle	0.02	0.01	0.05	80.07	0.41	0.25	0.11	11.20	0.07	0.00	7.80	0.00	0.02
DCS36	Jug, handle	niello	0.31	0.02	0.00	72.90	0.00	0.06	0.06	0.12	0.07	0.00	0.01	0.00	26.51

can be dated to the second half of the first century AD so it was satisfying to discover that both vessels were inlaid with copper sulphide niello. Because earlier analyses had been qualitative it was something of a surprise to see how much the niello applied to the two vessels varied in sulphur content. On the jug it contained 26.5% sulphur, corresponding to a mixture of digenite ($Cu_{1.8}S$) and covellite (CuS). The niello on the patera umbo has 17.3% sulphur and is mainly chalcocite (Cu_2S), possibly altered by corrosion. Despite this difference in composition, after nearly two millennia of burial there is virtually no difference in appearance; the inlay on the patera has a slightly richer tone but this may be simply because there is more of it.

The sample taken from the two-phase niello inlay on the upper section of the jug proved to be very suitable for microscopy and microanalysis, and so is the subject of this discussion. A general view of the microstructure is given in Figure 2, in which the corrosion of the surface of the inlay is plainly displayed, and a magnified image of the two-phase structure is shown in Figure 3. The equilibrium diagrams for Group 1B (Cu, Ag, Au) metal sulphide systems are an essential guide to the interpretation of the microstructures of niello such as this, but they can be extremely complicated (Villars et al. 1998). The Cu-S system is notably complex, with two monotectics, and several low-temperature phase transformations. Between the two monotectics there is a very narrow phase region which is δ-chalcocite and which melts at 1131°C. Either side of this is a trough; the one at the higher sulphur content is at 26 wt% sulphur and 814°C. This shows that a copper sulphide niello could be produced and used which was workable at temperatures similar to those of the silver sulphide acanthite (Ag_2S) which melts at 861°C.

The reaction in the trough is eutectic-like, but because of the presence of the miscibility gap to its right, is actually one liquid reacting to give a mixture of a solid and another liquid:

$$L_2 \rightarrow \delta + L_3$$

The second liquid is close to pure sulphur; the presence of this small amount of liquid may make the sulphide more pliable. There is then another reaction at 507°C where:

$$\delta + L_3 \rightarrow \delta + \varepsilon$$

and then a change in the δ phase to δ′ at 76°C. As it is likely the inlay was made first by forming small sheets and rods of the sulphide, cutting them out and then re-heating to apply them there is a possibility of a variety of final microstructures, a variety made more extensive by the existence of a number of metastable phases as well. Characterisation of this niello at this level is complex.

The niello on the patera is apparently slightly on the copper-rich side of the δ phase field and, in the absence of a suitable sample for microscopy, it is possible that we are dealing with an oxidised or corroded material. If not, then this niello would have become partially liquid at 1068°C, and probably more difficult to work than the higher-sulphur mixture on the jug. However, even at room temperature chalcocite has some ductility and it may well be usable at much the same temperature as the digenite/covellite mixture, or acanthite.

We should also consider the way in which the niello was manufactured in the light of the observation that Roman practice tended to link the basis of the metal sulphide and the substrate into which it was being inlaid, i.e. copper sulphide on copper alloys and silver sulphide on silver. The most usual method has been to react the metals with sulphur, a

process for which medieval recipes exist as far back as the Mappae Clavicula, parts of which possibly existed as early as the 8th/9th centuries AD. There is every reason to believe that this method was also used in Roman times, especially where analysis shows that alloys rather than pure metals have been reacted with sulphur to produce, say, a gold-silver-sulphur or a copper-tin-zinc-sulphur mixture or compound.

That an alternative might be possible is suggested by the occurrence of a form of copper sulphide at a small number of Romano-British sites. The product is usually interpreted as being matte, an intermediate in copper smelting. However, it has been reported at Silchester, at Colchester (Northover and Palk 2000) and at Hengistbury Head (Northover 1987), where it is very unlikely that copper extraction or refining was taking place. The matte found at Silchester was a coarse mixture of copper sulphide and the iron oxide wüstite, the sulphide component containing 26.5% sulphur. It differs from the niello we are discussing because it still contains iron up to the limit of solid solution (about 4%) and so would require separation from the iron oxide and, possibly, some refining. The matte at Hengistbury Head was almost free of iron but contained lead and silver. Despite these differences we should not ignore the use of by-products such as matte as a possible source of copper sulphide niello: the niello on the ewer has an iron impurity (0.31%) though the small amount of tin could well have come from corrosion rather than the reaction of copper containing some tin with sulphur.

The microstructure of the niello from the jug, as seen in Figures 2–3, is very clean but there are some inclusions of other materials, aligned by the process of working the niello into flat plates. Analysis of the inclusions by energy dispersive X-ray spectrometry in the scanning electron microscope revealed, besides the expected peaks for copper and sulphur, strong peaks for calcium and silicon and smaller but still significant peaks for arsenic, iron, potassium, phosphorus and aluminium. This would suggest that the inclusions could include calcium sulphate (gypsum, plaster of Paris), calcium phosphate (bone ash) and silica (sand) picked up in the workshop environment, perhaps an environment where fine metalwork and other crafts were being carried out. In these two examples the iron content is probably too low for the niello to have originated as matte.

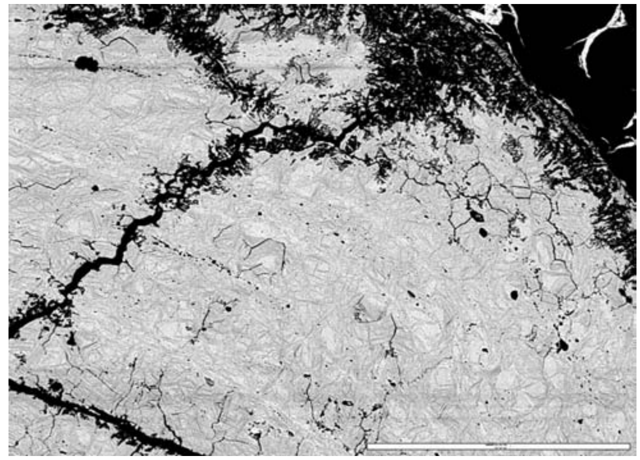


Figure 2: Backscattered SEM micrograph of a polished section of niello from the bronze jug. Corrosion within the niello appears black. Scale bar = 200 micrometres.

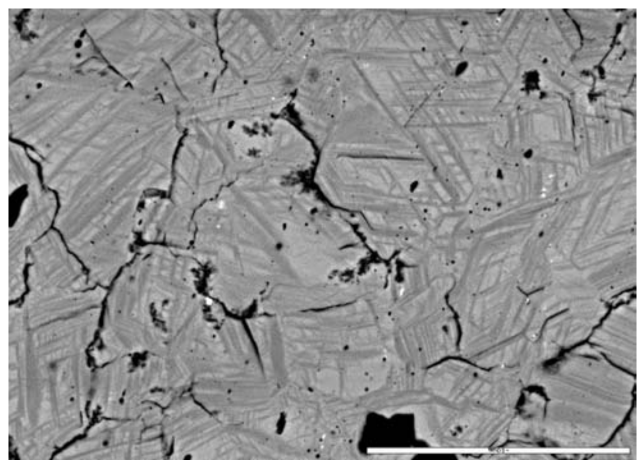


Figure 3: Detail of niello in figure 2. The directional alignment of the smaller inclusions (black) is a result of working the softened niello for inlaying. Scale bar = 50 micrometres.

A 4th century AD binary niello

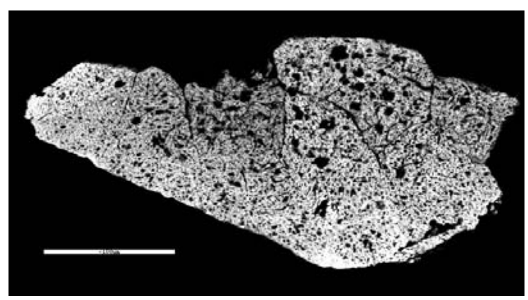
Apart from the Roman use of copper sulphide in the 1st century AD, the dominant form of niello in the earliest stages of its use was silver sulphide. With the exception of a mixed silver, copper and lead sulphide found on a 4th century BC silver rhyton from Trieste, N. Italy (Giumlia-Mair and La Niece 1998; La Niece 1998) the use of a single sulphide continued until about the 5th/6th centuries AD from when binary combinations, initially silver and copper, were adopted. An exception to this general pattern is when a binary combination is present because an existing alloy was reacted with the sulphur. The example described here comes from a gilt-silver mount in a hinged gold buckle plate of the 4th century AD (Fig. 4), which when examined qualitatively for the 1983 paper was recorded as a silver-gold sulphide.

A general view of the sample (Fig. 5) shows extensive porosity and cracking. At higher magnification (Fig. 6) the matrix has a mottled appearance. Qualitative analysis showed that the overall composition is a combination of silver, gold and sulphur. A point analysis of one on the brightest areas is given in Table 2. The principal elements (in atomic percent) were 68.2% silver, 14.0% sulphur, 17.4% gold. This is obviously not stoichiometric, and reveals the presence of un-reacted metal as well as sulphides. In the 1983 investigation X-ray diffraction analysis identified the presence of the gold-silver sulphide $AuAg_3S_2$ (utenbogaardite), perhaps to be correlated with the darker grey area in Fig. 5. The heterogeneity of this sample makes it difficult to determine an overall composition and this was not done. In the ternary silver-gold-sulphur equilibrium diagram (Villars et al. 1998) there is a minimum in the liquidus temperature at about 720°C so a properly constituted silver-gold sulphide niello would have a melting temperature below that of a plain silver-sulphide niello, although this was possibly an expensive way to achieve this. Perhaps another factor, if this is thought to be a deliberate choice of composition, is that it does have a good deep black colour, superior to the paler acanthite. Further qualitative analysis using energy dispersive X-ray spectrometry suggested that the sampled portion of this inlay is a mixture of acanthite with only a small amount of gold, utenbogaardite and un-reacted metal, which itself may be a mixture of silver and a gold alloy. Clearly, both silver and gold metal were used in the mix, and insufficient sulphur was added to react with all the metal. The temperature was not high enough to make the whole mass liquid, leaving an inhomogeneous spongy, sintered mass. The presence of specks of un-reacted gold alloy throughout the inlay contradicts any suggestion that silver-gold niello is an accidental result of in-situ reaction of silver sulphide with the gold substrate (Stemann Petersen 1994/5 144).

The mixture is what might be expected from a workshop making gold and silver jewellery, and it was remarkably free of other material, only a small amount of chlorine (from corrosion) and earthy materials was detected, suggesting clean workshop conditions.

An Anglo Saxon binary niello

In the 1983 paper it was reported that binary, silver-copper sulphide niello was identified as early as the



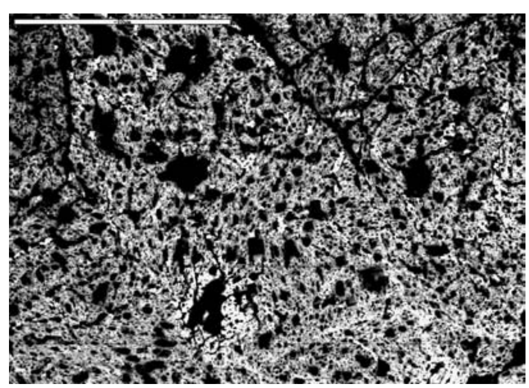


Figure 4 (left): Part of a gold buckle plate (4th century AD, British Museum AF 333). The silver-gilt central roundel, depicting an unknown emperor, is inlaid with niello. Figure 5 (top right): Back-scattered SEM micrograph of a polished cross-section of the niello from the gold buckle plate. Scale bar = 100 micrometres. Figure 6 (bottom right): Detail of the spongy sintered niello in figure 5. The overall composition is a combination of silver, gold and sulphur but the range of grey tones in the back-scattered image indicates a heterogeneous composition. Scale bar = 50 micrometres.

Table 2: Analysis of niello from a 4th century AD gold buckle plate.

Sample no.	Part	S	Cl	Fe	Cu	Zn	Ag	Sn	Au	Pb
					Weight %					
J367	bright spot	3.98	0.19	0.00	0.00	0.06	65.54	0.00	30.44	0.05
					Atomic %					
J367	bright spot	13.95	0.59	0.00	0.00	0.11	68.22	0.00	17.36	0.00

1st century AD in two silver plated brass horse-trappings from Fremington Hagg in Yorkshire. The inlay was identified as jalpaite (III$Ag_{1.55}Cu_{0.45}S$) which contains only about 13% copper by weight, little enough to have been included accidentally in a low purity silver alloy, for example a contemporary silver denarius from one of the more debased issues of Vespasian (Walker 1976). By the 5th century AD and on to the 10th century, a silver-copper sulphide was the type of niello most favoured, but the composition differed from that of the Roman example just cited. X-ray diffraction analysis showed that the preferred composition was roughly that of stromeyerite (AgCuS) with a higher proportion of copper to silver. When the niello from a brooch in a late Saxon hoard from Pentney (Figure 7) was analysed by XRD for the 1983 publication, the results were far from clear, though both copper and silver were identified by EDX. When a cross-section of the inlay was analysed quantitatively for this study, the reasons for the earlier problems became obvious.

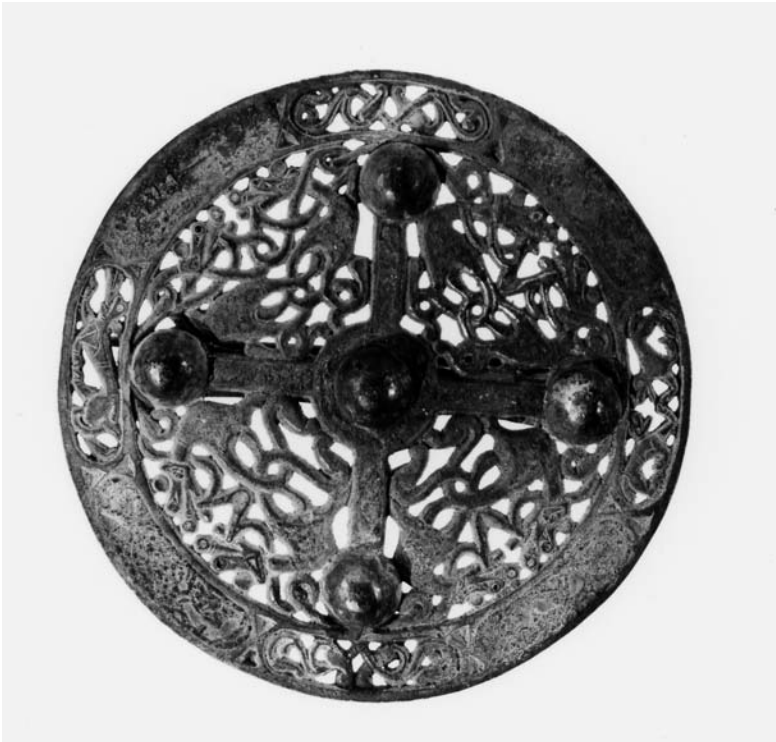
The whole cross-section of the inlay is shown in Figure 8 and a detail of the microstructure in Figure 9, both being back-scattered electron images obtained in composition contrast. Two features are at once noticeable: the first is a series of bands of inclusions which will be discussed later and which show us how the niello was pressed into the channel cut for it. The second is that the sulphide matrix is not homogeneous with possibly as many as three sulphide phases being present. Quantitative data from the different areas are set out in Table 3.

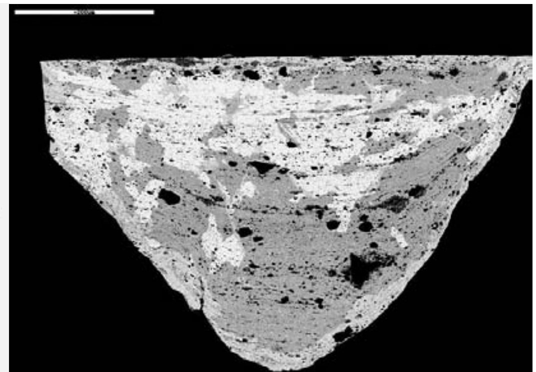
In the grey-scale of the images, the matrix of the sulphide mass appears dark grey. In both area (1) and point (4) analyses in Table 3 this has the composition of jalpaite already referred to in association to Roman copper-silver niello, so this inlay appears to be something of a throwback. In the image this appears slightly mottled so not all the material may have transformed to jalpaite, a low-temperature phase forming below 150°C. The sulphide phase which is palest (3) is not stoichiometric, being relatively rich in sulphur, but is close to the composition of acanthite. The mid-grey material (2) is intermediate in composition between acanthite and jalpaite. It has an acicular morphology, and may be metastable, not being readily identifiable from the equilibrium diagram (Villars et al. 1998). With the possible miscibility gaps in the Ag-Cu-S system it is not even certain that the liquid from which the niello solidified was homogeneous – it almost certainly was not – and, of course, it would also have been heat-treated when it was inlaid. The minimum liquidus temperature in the ternary system is of the order of 650°C. A final feature of the microstructure is a network of very bright inclusions which are rich in gold: possibly some of the silver used to make the niello was gilded.

The lines of inclusions are very distinctive and suggest two possibilities for manufacture. The inclusions are mainly silica, probably in the form of sand, and other earthy material, perhaps picked up from the vessel in which the niello was made or from a dirty surface in the workshop. The way the inhomogeneities in the structure cross several lines of inclusions could suggest that a sheet of inlay was made on a dirty bench by compressing together more than one batch of sulphide followed by heating. While the niello was still warm, a strip was cut and pressed down into the channel in the brooch. Alternatively the raw niello could have been ground into crumbs, pressed in in layers and heated with the application of each layer.

An 11th century AD ternary niello

In the 11th century AD, ternary niello, based on silver, copper and lead sulphides, appears to have been rediscovered. The first example identified in 1983 was a Byzantine silver-gilt amulet case of the 11th century followed by 12th/13th century examples in Russia and the Islamic world. Recently the opportunity has arisen to study in detail another early attempt at a ternary niello, inlaid in a magnificent lion's head door knocker created most probably in the 11th century in southern Italy or Sicily where Byzantine, Islamic and European cultures interacted (Meyer and Northover 2003). The knocker is illustrated in Fig. 10, with the niello a major feature of the design of the whole piece. In a detailed view of the niello (Fig. 11) a singular feature can be seen, an extensive distribution of white metal droplets.





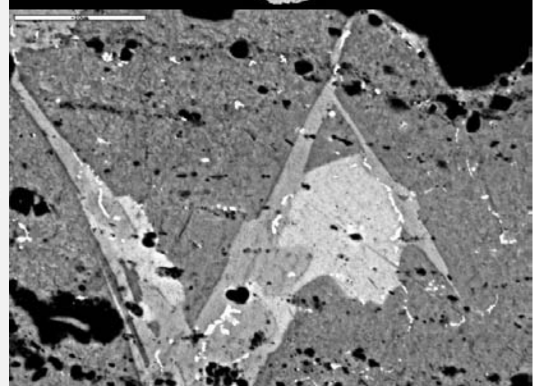


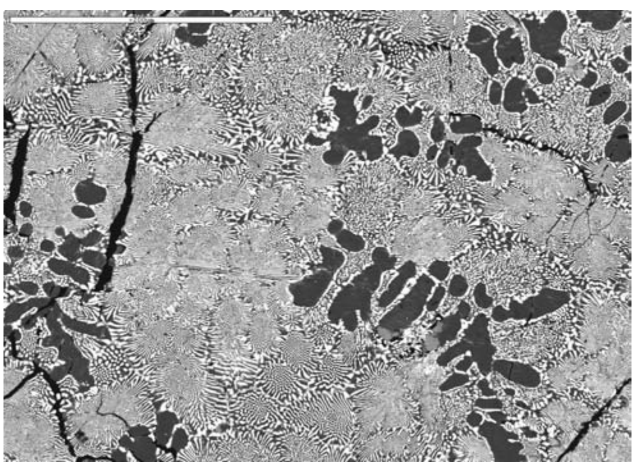
Figure 7 (left): Anglo Saxon silver brooch from Pentney, Norfolk, as excavated. The interlace decoration around the rim is inlaid with niello [British Museum 1980,10-8,3]. Figure 8 (top right): Back-scattered SEM micrograph of a polished cross-section of the niello from the brooch in figure 7. Bands of inclusions (black), which are mostly silica, show how the niello was pressed into the channel. The range of grey tones indicate inhomogeneity of composition. Scale bar = 200 micrometres. Figure 9 (bottom right): Detail of structures within the niello of figure 8. The network of bright inclusions are rich in gold. Scale bar = 20 micrometres.

Table 3: Analysis of niello from Anglo-Saxon silver brooch from Pentney, Norfolk.

Sample no.	Analysis	S	Cl	Fe	Cu	Zn	Ag	Sn	Au	Pb
					Weight %					
J262	1 dark area	12.35	0.00	0.15	13.08	0.36	73.99	0.00	0.00	0.24
	2 area	12.44	0.00	0.00	6.91	0.23	79.81	0.04	0.44	0.21
	3 mid-grey	15.27	0.08	0.02	1.29	0.00	82.18	0.07	0.17	1.09
	4 dark grey	13.12	0.05	0.01	13.07	0.10	73.32	0.04	0.30	0.10
	5 pale	15.37	0.00	0.02	1.18	0.26	80.54	0.09	0.18	2.45
					Atomic %					
J262	1 dark area	29.98	0.00	0.21	16.02	0.43	53.40	0.00	0.00	0.09
	2 area	31.23	0.00	0.00	8.76	0.28	59.57	0.03	0.18	0.08
	3 mid-grey	37.71	0.00	0.03	1.60	0.00	60.31	0.05	0.07	0.42
	4 dark grey	31.54	0.00	0.01	15.86	0.12	52.40	0.03	0.12	0.04
	5 pale	38.06	0.00	0.03	1.47	0.32	59.27	0.06	0.07	0.94

A fragmentary piece of the niello containing some of the white droplets was lifted with a scalpel and prepared metallographically. It consisted of a binary sulphide composition with significant corrosion at the surface, small metallic inclusions and a droplet of a lead silver alloy (see Table 4 for the composition of the knocker, and of the droplet). This led to an initial identification of the niello as a whole being a binary lead-silver sulphide composition. Subsequent re-examination of the niello in the scanning electron

Figure 10 (left): Copper alloy lion's head door knocker. Probably 11th century S. Italy or Sicily. Figure 11 (right): Detail of the surface of the door knocker. The niello inlay has an unusual appearance, with numerous pits and white metal droplets.



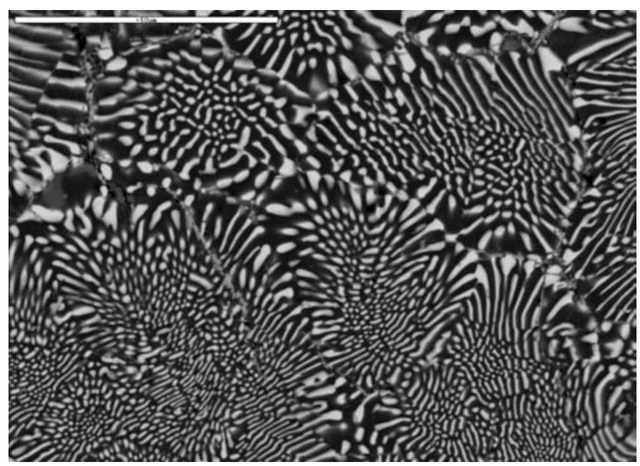


Figure 12 (left): Back-scattered SEM micrograph of a polished section of the binary niello from the doorknocker. It has an eutectic structure of copper and lead sulphides. Scale bar = 200 micrometres. Figure 13 (right): Detail of the eutectic structure in figure 12. Scale bar = 50 micrometres.

microscope has shown that this identification was incorrect (Figs. 12–13). The binary niello, which has a clear eutectic structure, turns out to be a mix of copper and lead sulphides with some lead-silver alloy inclusions and some small particles of a binary silver-copper sulphide. Silver is otherwise only present in the silver-lead alloy droplets.

This discovery can be linked to early recipes for niello. Biringuccio, writing in the 1530s and published posthumously in 1540 and translated by Smith and Gnudi (1990), describes a ternary niello being made by a silver-copper-lead alloy being poured into a flask containing flowers of sulphur. The flask was shaken until the mixture set. It was broken open and the contents ground. The ground sulphides are then applied to the area to be inlaid, heated with a blowpipe, pressed into place with a spatula and burnished. The eutectic temperature of the sulphide is of the order of only 550°C so that this heating would cause little damage to the surrounding bronze. There

Table 4: Analysis of an 11th century lion-headed door knocker.

Sample no.	Part	Fe	Co	Ni	Cu	Zn	As	Sb	Sn	Ag	Bi	Pb	Au	S
R1611/1	metal disc	0.00	0.00	0.02	93.07	4.17	0.00	0.00	2.39	0.25	0.00	0.10	0.00	0.01
R1611/2		0.01	0.01	0.00	93.58	4.15	0.01	0.00	1.86	0.18	0.00	0.13	0.07	0.01
R1611/3		0.00	0.00	0.00	92.30	4.05	0.00	0.01	3.22	0.29	0.00	0.14	0.00	0.00
R1611/4		0.00	0.00	0.01	93.05	4.17	0.01	0.03	2.43	0.23	0.06	0.01	0.00	0.00
R1611/5		0.03	0.01	0.03	91.71	3.94	0.00	0.00	3.22	0.41	0.00	0.65	0.00	0.00
R1612/1	droplet	0.00	0.00	0.00	0.55	0.00	0.00	0.66	0.00	84.52	0.00	14.20	0.06	0.01
R1612/2		0.00	0.01	0.01	0.38	0.00	0.01	0.44	0.00	64.11	0.06	34.86	0.12	0.00
R1612/3		0.00	0.00	0.02	0.38	0.00	0.01	0.55	0.00	74.58	0.02	24.36	0.09	0.00
R1612/4		0.00	0.00	0.00	0.33	0.03	0.00	0.48	0.00	56.97	0.01	42.11	0.07	0.00
R1612/5		0.00	0.00	0.00	0.27	0.01	0.02	0.33	0.00	50.04	0.00	49.33	0.00	0.00
R1612/6		0.00	0.00	0.04	0.57	0.00	0.02	0.67	0.00	88.39	0.01	10.21	0.09	0.00
R1612/7		0.00	0.00	0.01	0.29	0.00	0.00	0.42	0.00	60.15	0.01	39.10	0.00	0.01
R1612/8		0.00	0.01	0.00	2.01	0.42	0.00	0.44	0.00	65.78	0.03	31.26	0.05	0.00
R1612/9		0.01	0.00	0.00	0.44	0.01	0.00	0.60	0.00	75.64	0.02	23.20	0.05	0.03
R1612/10		0.00	0.01	0.00	0.69	0.00	0.02	0.87	0.00	92.21	0.08	5.90	0.23	0.00
R1611	disc/mean	0.01	0.00	0.01	92.74	4.10	0.00	0.01	2.62	0.27	0.01	0.21	0.01	0.00
R1612	droplet/mean	0.00	0.00	0.01	0.59	0.05	0.01	0.55	0.00	71.24	0.02	27.45	0.08	0.01

is a danger in niello containing silver sulphide, that if it is taken to too high a temperature in mildly oxidising conditions, it will decompose and silver droplets form, pitfalls well described in the 1983 paper. This could have happened here but the presence of so much un-reacted lead as well as silver indicates a more likely cause, that when the niello was made, insufficient sulphur was present for all the silver and some of the lead to react. We must also note that the niello was very clean and free of other inclusions, a good reason for supposing a clean method of manufacture, like that described by Biringuccio.

Conclusions

A combination of microanalysis and microscopy has enabled us to understand some of the anomalous inlays encountered in the research done in the early 1980s. We can now identify failings in manufacture with the 4th century gold-silver-sulphide and the 11th century ternary niello, and the success of the Romans in finding a copper sulphide niello which was as tractable as silver sulphide. The addition of insufficient sulphur to the metal to complete the reaction to sulphides (or loss of sulphur during the process) seems to have been a common problem. Meanwhile the inclusions describe the workshop conditions, while the micrographs define the extent to which niello is subject to corrosion.

The use of metal sulphide as an inlay material is undoubtedly attractive but it does not at first sight seem to be the most obvious material to use in this way. Metal sulphides do occur in nature, so they could have provided the original inspiration for niello, though no evidence has come to light for this as yet. Another potential source of sulphides was the by-products of processes such as metal smelting and purification. The possibility of matte being utilised as niello has been discussed above, though has not been proven. Gold refining with sulphur also produces metal sulphide by-products (Ramage and Craddock 2000). However, there is no evidence that the sulphur process for gold refining was used before the Renaissance so it cannot be put forward as an early source for niello. In the 1983 paper it was proposed that analytical evidence pointed to local workshops as the source for niello in the Roman and medieval periods: that scraps and filings from the workshop where the object was being made were used to make the inlay, rather than buying niello in from an outside source. The presence of gold throughout the section of the niello on gold items like the buckle discussed here supports that view. The picture for the earliest beginnings of niello is less well known, and detailed analytical study, particularly looking for impurities, could prove fruitful.

Microscopy of sections through these selected niello inlays confirms that inlay techniques were

adapted to the type of sulphide. Roman copper sulphide inlays appear to have been initially formed into sheets or rods, which were cut to shape then re-heated until at least partly ductile for application. This technique is also found on some Roman silver plate decorated with silver sulphide niello decoration (La Niece 1983: plate XLII). It is more related to wood or stone inlay work than metal inlay techniques such as enamelling, or indeed niello containing lead sulphide, as seen on the 11th century doorknocker discussed above. Lead sulphide niello mixtures were applied by melting, bringing the advantages of good bonding to the metal and a continuous, smooth surface with no gaps or joins, but the method had its disadvantages, as shown above.

There is still much to be done in the field of characterisation; there is considerable merit in pursuing phase identifications more fully in order to relate them to the equilibrium diagrams and thereby follow the formation of the niello. This detailed examination of four different types of niello inlays in decorative metalwork of different periods has helped illuminate several aspects of the evolution of the material and the ways in which it was made and applied, adding to our understanding of this once popular inlay technique.

Notes

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Chapter 15

From mine to microbe – the Neolithic copper melting crucibles from Switzerland

Th. Rehren[1]

Abstract

The occurrence of chalcopyrite in several late Neolithic crucibles from NW Switzerland and SW Germany has been variously interpreted as indicating evidence for local copper smelting, or being due to post-depositional phenomena. This study uses optical microscopy and a discussion based on textural and micro-stratigraphical arguments to demonstrate that chalcopyrite is a late formation and not indicative of copper smelting. This has significant implications for the technological and archaeological interpetation of these finds, but also illustrates the potential of image-based studies in science-based archaeology.

Introduction

The emergence and spread of metallurgy in Europe is a major concern of archaeological and archaeometallurgical research. In the 1960s scholars such as Renfrew and Branigan focused their attention – and consequently that of others – on the role which metals have played in the development of stratified societies and the emergence of elites, showing off with their access to these new materials. The Balkans and Western Asia are now both known to have had metallurgically competent Neolithic cultures, and issues of technology transfer and autochthonous developments between and within these regions and neighbouring areas are hotly disputed. Comparatively less attention has been placed on the early north-west Alpine metallurgy, although the Neolithic of northwest Switzerland and southwest Germany is characterized by the occurrence of several copper-using and copper-working cultures at a time when all surrounding cultures were still mostly a-metallic and showed no signs of metal working (Strahm 1994). In particular the Pfyn culture, dating to about 3800 to 3300 BC, shows considerable evidence for metal manufacturing, such as remains of crucibles and casting debris; but crucibles are also known from the subsequent Horgen culture (Fasnacht 1989). Startlingly, evidence for metal working in this region disappears after several hundred years, bringing these cultures back into line with their neighbours. Only after a further half a millennium or so metallurgy emerges again in Central Europe, heralding the beginning of the Bronze Age throughout the Continent. This time, it is a broad and sustained development with no particular emphasis on the Swiss or southwest German regions.

It is against this background that the crucible fragments of the Pfyn culture have attracted attention for more than a century, having been found at a wide range of sites and representing certainly several dozen different vessels. Despite their relative frequency and undeniable significance for our understanding of this truly Neolithic metallurgy, surprisingly little archaeometallurgical research has been done to properly characterise their precise place within the *chaîne opératoire* of copper metallurgy. Where, between the mine which provided the raw mineral, the various processing steps necessary to produce first copper metal and then useful metal artefacts, and their use, recycling and discard do they belong? One can – and should – debate how much scientific analysis really is necessary to address, possibly answer this question. W. Fasnacht, in a series of papers in the 1990s, has convincingly argued that they are casting vessels, processing existing metal stock; an assumption already manifest in their German name: *Gusslöffel* translates literally as ‘casting

spoons'. This interpretation is based on common sense as much as on careful observation, but stands against some results of high-powered instrumental analysis. Others, therefore, have suggested a possible alternative interpretation, based on the presence of copper-iron sulphides identified by X-ray diffraction analysis of some of the metalliferous residue on the inside of several of these vessels. In particular Maggetti et al. (1991) discuss whether the presence of copper sulphides, such as chalcopyrite, bornite and chalcocite, alongside metallic copper, indicates that smelting of sulphidic copper ore took place within these crucibles.

This debate is of major consequence for the interpretation of the Pfyn metallurgy: was it a fully autonomous and possibly independent development, mastering at an early stage the smelting of complex sulfidic copper ore, and if so, why did it disappear again after a few hundred years of apparently sustained exploitation? If, however, these crucibles really are mere melting and casting vessels, with no related evidence for the primary production of copper within the wider cultural context, then one could argue that this was copper manufacturing rather than producing. The metal then had to be obtained from outside the immediate cultural context via a long distance trade link, as no significant occurrence of native copper is known from the region.

Another potentially interesting aspect of this question relates to the still-enigmatic scarcity of early smelting slag throughout Central and Northern Europe, and the subsequent hypothesis of a slagless metallurgy (Craddock 1995). Here appeared a chance to literally look into a potential smelting vessel and finding out about the fate of the non-copper components of the ore when it is being smelted. This is particularly relevant in this case, where complex copper-iron sulfides are being put forward as the potential ore rather than the simpler and much richer copper salts such as malachite or atacamite. These latter minerals contain only volatile components besides the copper, rendering a slagless metallurgy just about conceivable, assuming that really pure ore was being smelted. The considerable amount of iron in minerals such as chalcopyrite or bornite, however, reaching up to parity with the copper content, has to be separated during smelting from the copper metal; here, the formation of some kind of slag or dross becomes inevitable, and should leave an archaeologically visible trace.

It is against this range of questions of regional archaeological significance and interest to the history of technology that a set of crucible fragments from northwest Switzerland were analysed; the results of the study are presented and interpreted below.

Materials and Methods

The archaeological literature knows several dozen contexts within the SW German/NW Swiss Pfyn and Horgen cultures yielding crucible fragments (Schlichtherle and Rottländer 1982; Fasnacht 1991). Despite a certain variability of their design, no systematic technological differences have so far been identified between crucibles from the two cultural units, or across the geographical extent of their occurrence. Thus, for the time being they are treated here as a single phenomenon, although later research may well lead to further subdivisions and subsequent re-assessment of the homogeneity of this group.

The archaeometallurgical study followed on from the initial ceramic study by Baumgartner (1982), published in parts by Maggetti et al. (1991). Samples of originally eleven crucible fragments, recovered during excavations of lake shore settlements and now in the care of the Swiss National Museum, became available for analysis. Offcuts of the pieces which were originally sampled for their ceramic composition were kindly provided by M. Maggetti in 1990, originating from Wetzikon (LM 10, LM 11), Wetzikon-Robenhausen (LM 2, LM 8), Stäfa-Uerikon (LM 5, LM 15, LM 16), Meilen-Schelle (LM 7, LM 14), Meilen-Fellmeilen (LM 12) and Gachnang-Niederwil (LM 13). Nine of these samples comprised also vitrified areas and opaque inclusions; LM 12 and LM 13 did not show any metallurgically relevant traces and were not studied further.

The offcuts were used to prepare polished thin sections which were then studied by reflected light microscopy and subsequently by scanning electron microscopy with energy-dispersive spectrometry.

Results

Nine of the samples were investigated, and a detailed description of the observations for each one is given in Rehren (2004). The focus of this current paper is on the archaeologically and metallurgically relevant aspects, and on some methodological issues. Thus, the results are presented in a summarized manner to avoid repetition.

A common feature of these crucibles is their very limited vitrification, which is typically restricted to a thin (typically less than one millimeter) layer on the concave surface of the fragments (Fig. 1). The remainder of the fabric is apparently unaffected by the heat of the metallurgical process(es) which took

Figure 1: Cross section through a crucible fragment from Stäfa-Uerikon. Note the very limited vitrification layer near the rim of the vessel, top left. Width of image ca. 3 cm.

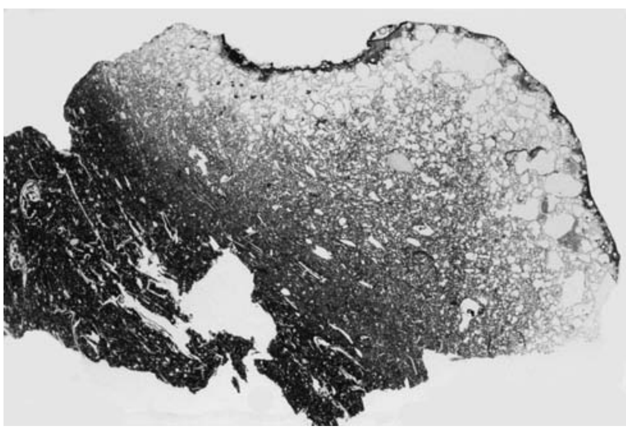
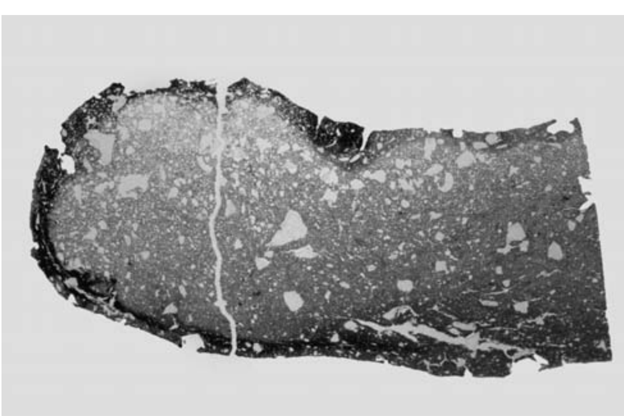


Figure 2: Thin section through a crucible fragment from Wetzikon-Robenhausen (Inventory number 32981 of the Swiss Landesmuseum*). Note the thick body, and the very limited vitrification layer near the rim of the vessel, top and right. Width of image ca. 3 cm.*

place in them, demonstrating that these vessels were heated from above / within. This is the norm for crucibles prior to the Iron Age (Rehren 2003), and does not in itself allow a more specific technological identification of the process(es) involved. In accordance with this, the bodies of the vessels are rather thick, up to several centimeters, and tempered with organic material (Fig. 2). This provides a thermally insulating matrix, clearly beneficial by minimizing heat loss through the body, and limiting to the top-most inner layer the potentially deleterious impact of the highest temperature on the mechanical integrity of the crucibles. Thus, the vessels can be made from ordinary clay with no particularly refractory qualities; the mechanical integrity is maintained even if the inside surface melts completely. This aspect of raw material choice and preparation is explored in more detail by Maggetti et al. (1991) and Maggetti (this volume), who found no indication for the selective use of a particularly refractory clay for the manufacture of these vessels.

An interesting feature is the evidence for repair, possibly re-use of some of the crucibles. At least in two instances was a second ceramic layer visible, covering an earlier partly vitrified surface (Fig. 3a, b).

The metallurgically crucial observation is the presence of copper-iron sulphides, identified in six of the fragments (LM 2, 5, 7, 8, 10 and 11). The same samples contain prills of metallic copper trapped in the vitrified ceramic, almost always in close proximity to the copper sulphides (Fig. 4 and 5). These sulphides, mostly identified as chalcopyrite, although chalcocine and pyrite occur as well, clearly equal those discovered in earlier studies by X-ray diffraction, both in these samples and in others. Their presence is central to the argument for copper smelting.



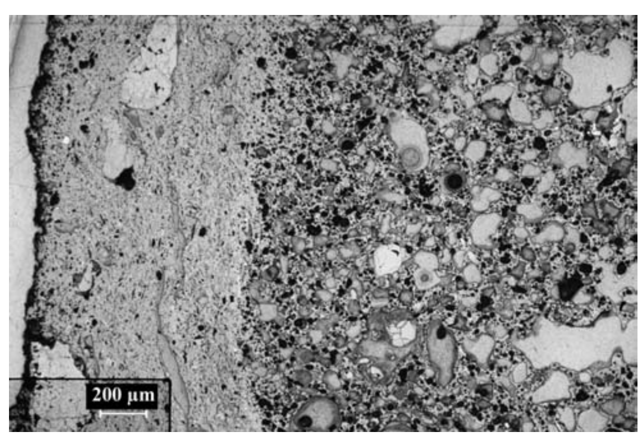
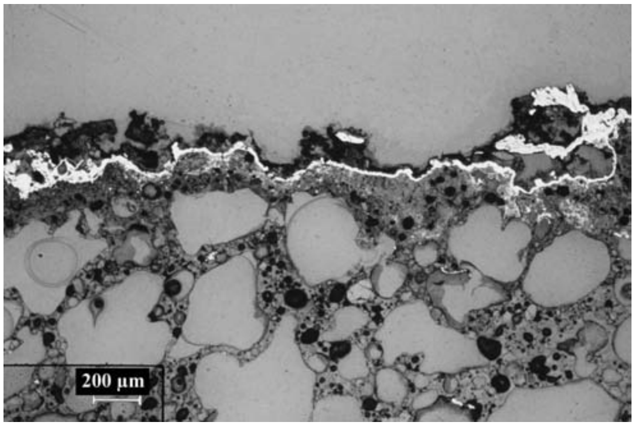
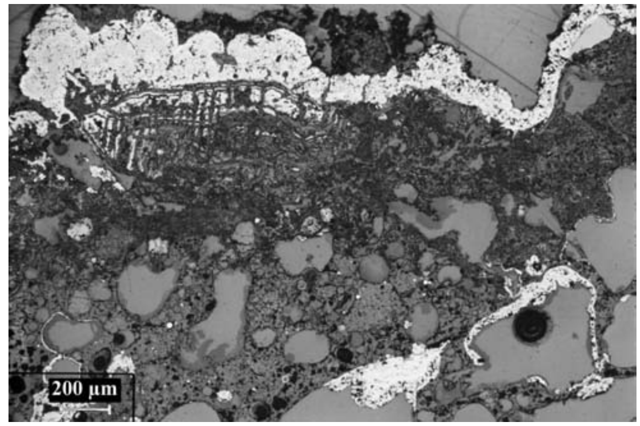


Figure 3a, b: Thin section of crucible fragment 36394 from Stäfa-Uerikon. Note the dark outer layer of a different ceramic, covering a previously vitrified surface. Width of thin section ca. 3 cm.





Figures 4 and 5: Micrograph of crucible fragment 32983 from Wetzikon. Their top surfaces are covered with a layer of chalcopyrite (yellow), partly with a cauliflower-like structure.

In addition to the chalcopyrite found within the vitrified areas of most crucibles, several fragments have a scatter of small pyrite clusters throughout their ceramic body. Each cluster comprises several dozen tiny crystals, together loosely arranged in a sphere of less than 0.1 mm diameter. Such structures are known in ore petrography as *framboids*, from their perceived similarity to raspberries (in French *framboise*), or petrified bacteria, from their assumed origin (Ramdohr 1975). They are typical of sulphur-bearing anaerobic environments, such as siltstones and slates rich in organic matter. Framboids were found in four or five of the samples (LM 7, 11, 14 and 16, and possibly 10).

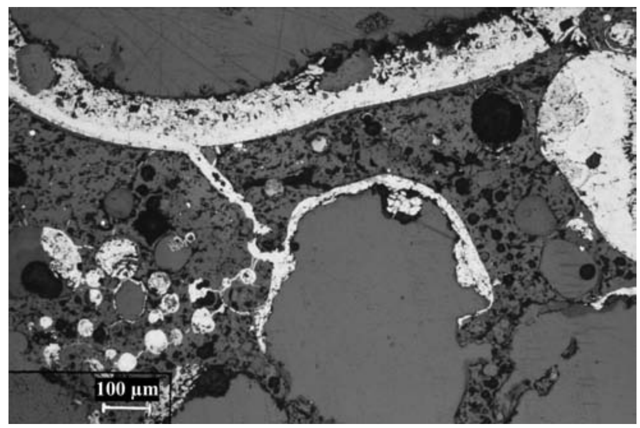


Figure 6: Micrograph of crucible fragment 32983 from Wetzikon. The chalcopyrite covers not only the surface and the inside of a gas bubble, but also fills a crack connecting the two.

Spatial aspects of sulphide and metal occurrence

The presence of copper sulfides is restricted to the vitrified parts of the crucibles, as one would expect if they constitute ore remnants, and where they occur in close proximity to the prills of metallic copper and copper oxide dispersed and dissolved in the vitrified matrix (see below). Despite this close proximity to the copper metal, there is, however, an important systematic difference between the spatial arrangement of sulphides and metal. The copper metal is inevitably present as droplets trapped in the vitrified ceramic; the metal was therefore obviously at the same time liquid as the ceramic layer in which it is embedded. The sulphides, in marked contrast, populate the surface of the vitrified ceramic, often lining the inside of gas bubbles which result from the decomposition of the clay minerals during vitrification ('bloating' of the ceramic). Most tellingly, cracks in the vitrified ceramic are often cemented by copper sulphides (Fig. 6). Another fundamental difference between copper metal and sulphide inclusions lies in their shape; the metal is inevitably present as prills, i.e. small almost perfect spheres typical of liquid metal solidifying in a viscous surrounding (Fig. 7a, b). In contrast, the sulphides are without exception showing a layered structure wrapping the ceramic matrix, often with a cauliflower-like upper surface and only ever appearing in a spherical shape when filling spaces which clearly are former gas bubbles; semi-filled such bubbles illustrate the gradual process by which they were filled. In effect, and while at present copper metal and copper sulphides co-exist within the very same space, there is a clear stratigraphic separation between the two (Fig. 8). The copper metal can only have been incorporated in the ceramic matrix while it was hot to the level of

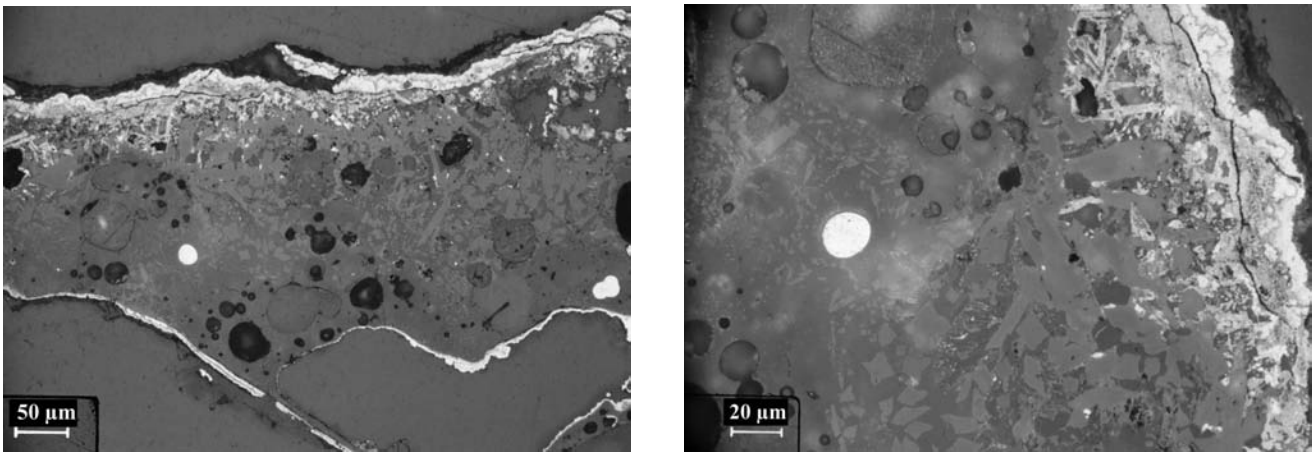


Figure 7a, b: Micrograph of crucible fragment 32982 from Wetzikon. The surfaces are covered by chalcopyrite; the two bright prills (centre left and far right) are metallic copper, embedded deeply in the vitrified ceramic. The closeup on the right clearly shows the difference between the copper droplet (centre left) and the chalcopyrite (right) replacing the corroding vitrified ceramic.

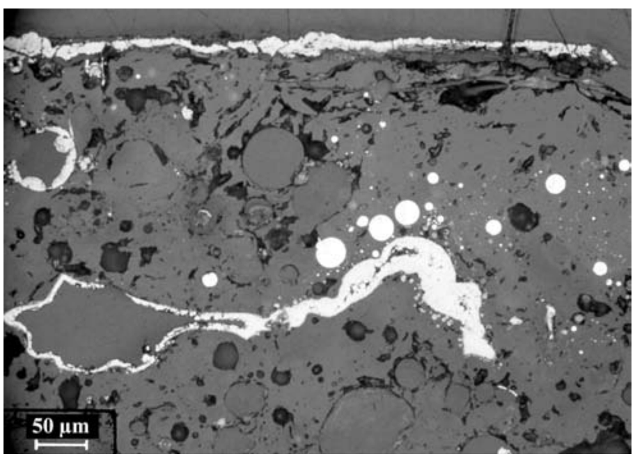


Figure 8: Micrograph of crucible fragment 32983 from Wetzikon. The copper prills (bright, centre to right) are within the vitrified ceramic, while the chalcopyrite is on its surfaces, both internal and external.

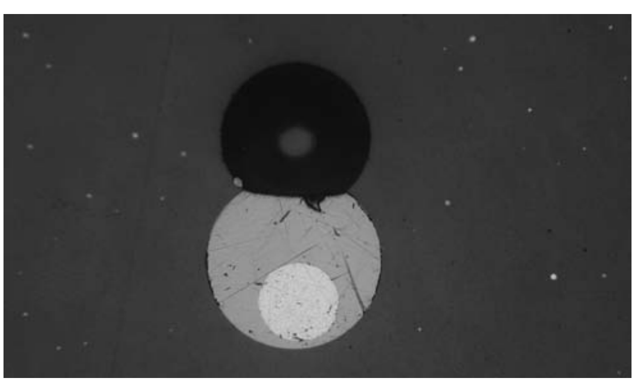


Figure 9: Micrograph from a Mexican copper slag, showing a copper/copper sulphide prill suspended in the melt by an attached gas bubble.

vitrification, while the sulphides can only have been deposited here when the vitrified ceramic was cool enough to allow cracks to form in the glassy parts, and by a mechanism uniformly cladding external surfaces and the inside of bubbles, which are often visibly connected with each other and the surface by a network of cracks.

However, the combination of sulphide inclusions and gas bubbles frequently is found in copper smelting slag (Fig. 9). In those cases, however, the sulphides form prills attached to gas bubbles, which most likely form from the reaction of the sulphide with oxygen provided by the siliceous slag, resulting in the formation of sulphur dioxide and copper metal. These sulphur dioxide bubbles provide the buoancy necessary to keep the matte prills afloat in the slag; accordingly, matte and gas form two semi-detached spheres, quite different from the concentric spheres of chalcopyrite cladding the inside of air bubbles as is the case in the Pfyn crucibles.

Textural and phase issues

A further significant aspect is the correct identification of the sulphides present in the Pfyn crucibles. They have previously been identified by XRD as chalcopyrite, and ore microscopy has confirmed this identification. However, chalcopyrite can originate from a number of formation processes. While these processes produce a phase of identical composition and fundamental crystal structure, they often result in quite different morphologies and textures, which are in turn indicative of the respective processes.

The most common texture of chalcopyrite ore relevant to ancient smelting is that of rich hydrothermal ore deposits, where the mineral forms well-developed crystals and aggregates, often intergrown with other sulphides such as pyrite, galena and sphalerite, and gangue minerals such as quartz, barite or calcite. The grain size of these crystals ranges from several centimeters down to a few micrometers, and they are typically either exhibiting their characteristic crystal forms or have more or less straight boundaries with their neighbouring minerals. Ancient smelters apparently preferred more coarse-grained ore which they could more easily concentrate by crushing and sorting, but finer-grained minerals are often intergrown with each other and survive as tailings or other waste materials near the mine and the smelter.

In the material studied here, the chalcopyrite forms layered structures and spheroidal aggregates of needles pointing outwards from a nucleus; the combination of these two textures results in the cauliflower-like pattern which predominates in these samples when the chalcopyrite layer borders on one side to void space. This texture is indicative of low-temperature, often aquatic environments of sulphide deposition, such as are prevalent in certain submarine-exhalative or sedimentary ore deposits (e.g., Ramdohr 1975).

In contrast, matte inclusions, i.e. artificial copper-iron sulphides from metallurgical contexts, have a texture typical of solidification from a melt phase, including the decomposition of a high-temperature solid solution crystal into a matrix of bornite with lamellae of chalcopyrite or *vice versa*, depending on the exact copper to iron ratio, and eutectoid structures of matte with magnetite, reflecting the iron and oxygen content in the system (e.g., Bachmann 1982). These latter structures are extremely rare in nature, while they are the norm in copper slags and other artificial contexts involving base metal sulphide melts.

Smelting or melting?

The investigation so far has demonstrated that there is likely a chronological gap between the incorporation of the copper metal into the vitrified ceramic, which is obviously contemporaneous with the high-temperature activity which took place in these crucibles, and the formation of the chalcopyrite, which has been deposited only after the material had solidified and cracks had formed in the vitrified ceramic. Furthermore, the texture of the chalcopyrite is indicative of a low-temperature formation, probably within an aquatic environment. Thus, there is evidence for the presence during the use of the crucibles for metallic copper, while the chalcopyrite has formed later, probably only during the deposition of the crucibles in the archaeological layers. This temporal division makes it very unlikely that the chalcopyrite represents residual ore of a smelting operation.

A further argument against chalcopyrite smelting is the lack of an enhanced iron oxide level in any of the vitrified material; unpublished EDS analyses of the vitrified ceramic of these crucibles match closely the composition of the un-vitrified ceramic matrix, with the exception of an elevated copper content in the vitrified material. If chalcopyrite ore would have been smelted in these crucibles, one would expect a noticeable increase in the iron oxide content of the siliceous phase, effectively making it a metallurgical slag rather than vitrified ceramic material. Such an increase in iron oxide contents in the siliceous materials on the inside of vitrified crucibles has been found both in Early Bronze Age copper smelting crucibles from Shahr-i Sokhta in Iran (Hauptmann et al. 2003) and in Chalcolithic crucibles used to smelt arsenical copper in SE Spain (Müller et al. 2004). While the absence of evidence rarely is evidence for absence, it is difficult to see in this case how chalcopyrite can be smelted to copper without significantly enriching the surrounding melt in iron oxide.

The origin of the chalcopyrite

It is relatively straight forward to exclude copper smelting, based on the microscopic evidence presented; this leaves, however, the necessity to explain the presence of significant amounts of chalcopyrite within the metallurgically relevant areas of the crucibles. The occurrence of chalcopyrite in nine out of eleven samples is clearly a significant observation, given that these eleven samples were initially taken with a ceramological study in mind, not a metallurgical one. On the other hand, it is a phenomenon apparently characteristic of the Pfyn crucibles; I am not aware of any other copper crucibles having been reported to possess such chalcopyrite layers.

The key to their understanding lies in the particular texture, identified earlier as indicative of a low-temperature, possibly aquatic, origin, in combination with the small *framboid* aggregates of pyrite crystals which were found dispersed throughout several samples. We know that the crucible fragments were excavated from lake settlements, where they were embedded for millennia in the silty sediments. These sediments were often anaerobic, as is indicated by the

frequent preservation of organic material such as wood, which makes them archaeologically very exciting. In these anaerobic conditions thrive bacteria which base their metabolism on the processing of sulphurous compounds, resulting in the deposition of metal sulphides as a metabolic waste product.

Without having explored in detail the biochemical mechanism responsible, it is reasonable to assume that the slow corrosion of the metallic copper trapped in the vitrified parts of the crucibles, together with the release of iron ions from the weathering glass matrix, provided a supply of metal ions into the surrounding aquatic anaerobic environment, where these ions reacted with the sulphide ions provided by the bacteria to precipitate as chalcopyrite. In those parts of the crucibles where no copper metal was present, and hence no copper ions available, we accordingly find only pyrite aggregates. The much increased quantities of sulphide precipitation in the vitrified areas compared to the not vitrified parts of the crucibles most likely results from the much increased release rate of metal ions due to the increased corrosion rate of the vitrified ceramic compared to the non-vitrified ceramic.

So what?

The hypothesis of copper smelting can be safely ruled out for the Neolithic crucibles of the Pfyn culture. Instead, a much more convincing alternative model is proposed to explain the presence in these vessels of chalcopyrite together with copper metal. This shift in interpretation has several ramifications, two of which I want to stress in this context; one relates to the archaeological interpretation, while the other is of methodological concern.

Firstly, the presence of metal artefacts and the apparently local ability to melt and cast copper demands a discussion of the origin of the metal as much as that of the metallurgical skill. It is beyond the scope of this paper to speculate on either of these, but it is clear that the former is probably best addressed in the context of a typical metal provenancing study, using lead isotope ratios and trace element studies (Rohl and Needham 1998). The relatively rich data sets available for the period, particularly for the Balkans as one of the main potential supply regions (Pernicka et al. 1993, 1997), should make this a feasible task. The other is more difficult to address scientifically; too little comparative data is available at present to consider 'technological styles' or similar approaches to distinguish between potential directions of transfer of knowhow. It may suffice here to suggest that the Pfyn metallurgy was probably based on imported copper metal, obtained probably via a long-distance trade link which at some point in time failed, spelling the end to this secondary metallurgy. A similar case of a regional metallurgy being based on imported copper alone is known f.i. from contact period Canada, with the Inuit manufacturing a range of implements from European brass kettles (Moreau and Hancock 1996).

An important aspect of this study, significant well beyond the immediate chronological or regional framework, is the apparent strength of optical methods, common sense and an open mind when considering the seemingly firm and indisputable results obtained by advanced scientific instruments. Archaeology is a historic science where relative and absolute time are important factors, while many scientific approaches are based on the actualistic paradigm that time has no influence on the validity of measurements or laws of nature. Despite this, science-based archaeological approaches have to consider the impact implicit in the chronological dimension of archaeology. The situation present now is the cumulative result of different processes, and these have to be seen in a quasi-stratigraphic sequence. Any instrumental analysis will only describe the *status quo*, without chronological depth. This is equally important for issues of technological processes lasting only minutes or hours, and for the effects of corrosion and post-depositional changes taking place over several millennia. Of the many analytical methods nowadays available to the archaeometrist, image-based approaches are still best suited to take into account aspects of contemporaneity and sequentiality.

Acknowledgements

My first thank has to go to Mike Tite, who welcomed me early on in my career into the fold of the archaeometrical community, and has been encouraging and supportive ever since. His pragmatic and enthusiastic attitude towards a wide range of research avenues within archaeometry have been an inspiration for me for the last 20 years.

I am very grateful to Marino Maggetti for allowing me access to the material, and to Walter Fasnacht for valuable background information and discussions. Andreas Ludwig of the German Mining Museum admirably prepared the polished thin sections to a quality without which this research would have been difficult to achieve. This study was carried out while the author was at the German Mining Museum in Bochum, funded by a grant from the Volkswagen Foundation in Hanover to set up the archaeometallurgy laboratory at that museum.

Note

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Chapter 16

Across the wine dark seas… sailor tinkers and royal cargoes in the Late Bronze Age eastern Mediterranean

Z.A. Stos[1]

Abstract

The Late Bronze Age (c. 1600–1100 BC) in the Eastern Mediterranean was a period of high prosperity and relative ease of movement. The metallurgy based on tin bronze was highly developed and silver was highly prised, as is demonstrated by contents of the Shaft Graves in Mycenae and the wealth of grave goods on Crete. In the same period copper smelting on Cyprus was at its height. The identification of patterns of the centres of metal extraction and the trade in metals in this period represents the earliest European industrial network. One of the questions often raised is that of the type of entrepreneurship that drove the metal trade: was it monopoly of the kings who exchanged bulk metal as expensive gifts, or was it a small man's way of making a living? Two LBA shipwrecks excavated in the second half of the 20th century off the coast of SW Turkey by the team from the INA under the directorship of George Bass provide the richest finds of copper and tin traded in the 14th and 13th centuries BC in this region. Both of them – Uluburun and Gelidonya – carried large amounts of copper and tin ingots, as well as numerous other metal objects. However, the cargo of these two ships has very different character, while the Uluburun with 12 tonnes of metal on board, massive amount of new pottery, raw ivory and glass ingots can be regarded as 'royal', the finds from Gelidonya fit the description of a travelling metal smith. This paper will examine the shipwreck and land site evidence for the relationship between the origin of LBA Mediterranean copper ingots and copper-based artefacts based on the results of research carried out in the Isotrace Laboratory at Oxford under the directorship of Noel Gale and the author. Crete, an island without its own Late Bronze Age copper extraction industry and therefore relying on the ships bringing the metal, was chosen as the focal area for this study.

Introduction

The wealth of copper based metal artefacts excavated in the 20th century in Greece, Cyprus and the Near East in the LBA context is quite considerable, if indeed it represents only a small fraction of the metal that circulated then in this region. The earliest excavation of the Palace of Knossos on Crete and other contemporary sites around the Eastern Mediterranean led Arthur Evans to conclude that in the earlier phase of this period (LMI) the area was under the Minoan Thalassocracy, in many ways similar to colonial Britain in the 19th century (for discussion see: Hagg and Marinatos, eds. 1984). Since Crete is not known for its wealth of copper ores (Gale and Stos-Gale 1986; Stos-Gale 2001) it has been widely believed that the Minoan expansion was in some way spurred by the need to control the Cypriot copper mines. Similar conclusions have been drawn as to the Mycenean expansion in the later part of the LBA (Catling 1964; Dickinson 1977).

For the last 20 years of the 20th century all the archaeological theories about the sources and trade in metals in the eastern Mediterranean came under the scrutiny of lead isotope provenance method. This method of identification of sources of raw materials depends very strongly on the available comparative

database (Gale and Stos-Gale 1982, 2000). While strongly criticised by scientists and archaeologists alike (for defence of LI: Tite 1996) the Isotrace Laboratory at Oxford was until 2001 turning out large numbers of data for Bronze Age metals and related minerals collected through geological and archaeometallurgical surveys.

The largest amount of LBA copper samples came from the two shipwrecks: Gelidonya (Bass 1967) and Uluburun (Bass 1987; Pulak 1998) that sank along the south-eastern coast of Turkey at the end of the 13th and 14th century BC respectively. The Uluburun ship carried 360 copper and 160 tin ingots weighing in total about 12 tonnes, which are the most spectacular metal finds in a time capsule of around 1307 BC. A smaller ship, dated to 1200 BC was excavated by George Bass and Peter Throckmorton in 1960 near the Cape Gelidonya. The cargo of this ship consisted of about 100 pure copper ingots and their fragments and more than 100 tin bronze tools, some of them only roughly cast and unfinished, as well as metal rods and sheet fragments. With this cargo there were also found smith's tools, stone hammers, polishers, a whetstone, a swage and an anvil. Clearly this ship was a travelling workshop of small entrepreneurs, a sailor smiths and tinkers, who travelled along the coast collecting and supplying precious bronze to the inhabitants of the towns and settlements. The identity of these tradesman has stimulated much discussion at the time (Bass 1991). Lead isotope analyses of over 200 samples of copper-based metal from this ship allowed to identify sources of this assemblage and compare it with the sources of copper used at that time in the Aegean, on Cyprus and the Near East. This study cannot answer all questions about the metal production and distribution in the LBA eastern Mediterranean, but it is hoped that it will provide a useful contribution to the discussion.

So far no other Bronze Age shipwrecks with so much metal cargo have been found, but it is quite possible that a similar ship brought a load of Cypriot copper oxhide ingots to the settlement of Mochlos on Crete in the late 15th century BC (LMII) (Soles and Davaras 1994 and 1996; Stos-Gale 2004), and another one called in a Sardinian port at the end of the LBA (Gale and Stos-Gale 1987; Stos-Gale and Gale 1997). There are also traces of Bronze Age shipwrecks carrying copper and tin off the coast of Israel (Wachsmann and Davis 2002) and a cargo of copper oxhide ingots has been found in the sea off the cliffs of east Euboea near Kyme bay facing the island of Skyros (these ingots are in the National Archaeological Museum, Athens).

The methodology of provenance studies in the LBA eastern Mediterranean

The current database of lead isotope and elemental analyses of Bronze Age metals and ores in Oxford (OXALID) has been assembled over more than 20 years of research. The Isotrace Laboratory produced over 2,000 lead isotope analyses of ore and slag samples collected during numerous archaeometallurgical and geological surveys in Greece, Cyprus, Italy, Spain and Bulgaria. The methodology of the Thermal Ionisation Mass Spectrometry (TIMS) analyses in the Isotrace Laboratory has been described previously (Stos-Gale et al. 1995a). Together with the relevant lead isotope data published by other researchers it forms a database of over 2,600 entries that can be used for comparisons with the Mediterranean Bronze Age metals. This amount of data seems quite substantial, but unfortunately there are still very important gaps including Egyptian and Middle Eastern ore sources (for full bibliography of LI data related to provenance studies see Gale and Stos-Gale 2001).

The great advantage of using TIMS for lead isotope analyses is the full comparability of the data obtained in different laboratories. It is hoped that future lead isotope measurements, which most likely will rely more often now on the new generation of mass spectrometers with a laser ablation source (Multicollector Inductively Coupled Plasma Mass Spectrometry: MC-ICPMS), will be standardised for comparability with the TIMS data. Preliminary comparisons of TIMS and MC-ICPMS lead isotope results show that this new technique, in spite of very high instrumental accuracy, is capable of producing sets of data that cannot be directly compared with TIMS results (Baker et al. 2002).

Tables 1 and 2 summarise the data used for interpretation of the Bronze Age copper based metals discussed in this paper. Only few of the lead ore occurrences in the Mediterranean do not have associated copper ores (for example: Cycladic island of Anaphi, Elba, some of the Bulgarian and Egyptian sites). The LI data for these ores was excluded from the comparisons.

For the interpretation of the results of our lead isotope analyses of the Bronze Age Eastern Mediterranean metal artefacts we use two simple methods of comparisons. Firstly, Euclidean distances in the three-dimensional space with axes defined by the three lead isotope ratios are calculated between each of the artefact results and all currently available lead isotope data points for ore and slag samples. In certain cases this approach shows that many ore samples from

Table 1: Lead isotope analyses of copper and lead ores, and copper slags obtained in the Isotrace Laboratory relevant to the metal trade in the Bronze Age Mediterranean.

Country	Region	Ores	Artefacts
Greece	Aegean Islands	444	541
Greece	Mainland	353	819
Greece	Crete	61	694
Cyprus	Troodos	430	478
Near East	Iran, Egypt, Syria, Israel	96	451
Turkey	Sites on and off the Aegean coast	60	1095
Spain	South Spain and Menorca	101	219
Italy	Sardinia, Elba, Liguria	332	339
Bulgaria	South-East	147	364
	Total	**2,024**	**5,000**

Table 2. Summary of published LI data on ores and slags included in OXALID.

Country	Regions	Number of LI data	Publication
Iran	Central Iran	27	Barns, National Bureau of standards (currently NIST) unpublished data
Jordan	Arabah, Feinan	40	Hauptmann et al. 1992
Saudi, Egypt, etc.	Red Sea coast	74	Stacey et al. 1980, 1983
Turkey	Troad, Black Sea coast, Malatya, Taurus	321	Wagner et al. 1989-1991 and Hirao et al. 1995, Yener et al. 1991

two or three geographically different regions have all three lead isotope ratios identical with an artefact, within the limits of the analytical error. Therefore the second stage of interpretation of the data must include the comparison of data on two-dimensional plots of LI ratios, to assess the patterns of distribution of all ore data points for each of the deposits in relation to the data points representing the artefacts. Finally, the geochemistry and history of exploitation of the ore deposits identified as possible sources has to be checked. Usually at the end of these procedures all but one ore source can be eliminated.

It is quite possible that some of the artefacts were made of re-melted metal, but the pattern of all lead isotope data indicates that this practice will have mostly little effect on the conclusions, because the great majority of metal used in the Bronze Age Aegean originated mostly from a few local copper and lead/silver occurrences. Further discussion of mixing is given below.

Copper ore sources used in the Late Bronze Age Mediterranean

The identification of copper ore deposits exploited in the Bronze Age Mediterranean world has been a central topic of research of archaeologists and archaeometallurgists for more than 30 years. Surveys of copper deposits in Greece, Turkey, Serbia, Bulgaria, Iran, Jordan and Israel, as well as the Eastern Mediterranean, brought much information on this topic, and the question posed by Bass in 1967: W*here were these copper mines and smelting places?* (p. 76–78) can be now discussed with at least some field evidence.

Additionally, the LI analysis, however much disputed in some aspects, leaves no doubt as to the origin of the majority of existing oxhide ingots. It is Cyprus, and moreover, the data indicates that the majority of ingots that could be dated to the 12th c. BC or later, were made from ores mined in the Solea region in the north-west part of the island (Stos-Gale et al. 1997; Gale et al. 1997). There is no doubt also that the oxhide (and large bun) ingots are cast from primary, smelted, but unrefined, 99% copper. The metallurgical structure of these ingots leaves no doubt that they have not been made by re-melting copper; all of them have very characteristic appearance of the fleecy top surface, smooth, if pitted bottoms and internal large gas cavities. All these characteristics cannot be achieved beyond the primary copper extraction. The primary copper smelting in the LBA is an activity that would produce a reasonable amount of copper slag. Ancient copper slags are found in great quantity on Cyprus (Stos-Gale et al. 1998b). The overwhelming majority of slags in the fields and near the mines has not been dated, so it is impossible to identify those that might have been related to the Bronze Age copper production, but on the other hand it is difficult to exclude the possibility

that some of them are of this period. In recent years, a small slag heap in the location called Phorades, near the Mitsero village has been excavated and a Bronze Age date for this activity was suggested (Given et al. 1999, 2003). Many other slag heaps scattered around Cyprus might contain at least one stratum dating to this period.

The other suggestions discussed in 1967 by Bass, namely production of oxhide ingots on Crete, near Kyme and on Sardinia, can be now forgotten. Copper ores on Crete do not occur in any exploitable quantity, even by Bronze Age standards. Since the EBA the main sources of copper for the Minoans were the Cycladic Islands and Lavrion in Attica (Stos-Gale 2001). The very small amount of copper smelted in EMII at Chrysokamino, a cliff-top in the Mirabello Bay, was based on ores brought there from the Cycladic islands (Stos-Gale 1998). Another site mentioned by Bass, Kyme bay on the island of Euboea where a cargo of oxhide ingots was found (Gale 1991), might have been a landing place for boats, but there is no evidence of copper smelting anywhere on Euboea and small outcrops of copper ores in the high mountains in the south of this island have only been discovered recently (Gale and Stos-Gale survey with IGME in 1993). Apart from the Cyclades and Lavrion, the important copper (and copper slag) occurrences in Greece are in Chalkidiki and in the Othrys and Rhodope mountains. However, there is very little evidence of Mycenean presence in these regions before the Geometric period (for summary see Gale and Stos-Gale 2000).

Copper was certainly extracted from local ores in the Late Bronze Age on Sardinia, and various ingot fragments, as well as a number of artefacts made of this copper were found on Sardinia. However, the LI evidence leaves no doubt that the oxhide shaped ingots, together with Cypriot tripods and pottery, are of Cypriot copper (Stos-Gale et al. 1997). However, it is important to remember that copper ores on Sardinia are not as common as lead ores (some of them also containing silver) and lead with Sardinian LI ratios has been identified in numerous LBA sites on Cyprus and in Ugarit (Stos-Gale and Gale 1994 and unpublished Isotrace data).

The Hittite empire was famous for its metalwork and there are a number of very rich copper deposits in modern Turkey that might have been exploited in the LBA. Most often mentioned in the archaeological literature is Ergani Maden, in the south-east part of Turkey near Elazig. Metal from this mine is certainly in evidence amongst the local prehistoric finds (research of A. Çukur and A. Kunç, analyses done in the Isotrace Laboratory, unpublished). Other important copper mining regions are on the south-east part of the Black Sea coast (Wagner et al. 1989). Very interesting copper, lead/silver and possibly tin sources might have been exploited in the Bronze Age in the Taurus Mountains in southern Turkey (Yener et al. 1991). Much archaeometallurgical work has been already done in Turkey, but quite clearly much more needs to be done. Hittites played an active part in the eastern Mediterranean network of the Late Bronze Age regional powers and there is still very little scientific evidence for their exploitation and trade in metal sources. It is quite possible that much of their metal was going to Egypt as the scanty evidence of LI analyses of metal from Amarna indicates (Stos-Gale et al. 1995b).

Other LBA copper mines in this region are in the Wadi Arabah divided between Israel and Jordan, Timna (Rothenberg 1990) and Feinan (Hauptmann et al. 1992). Both regions have been extensively excavated and are run as cultural heritage sites open to the public. There is also LI evidence that the copper from these mines was circulating in the Eastern Mediterranean in the BA (Stos-Gale et al. 1995b, 2001).

In Greece the copper deposits are much smaller than in Anatolia, but it seems difficult to deny that the mining region of Lavrion in Attica was used for copper production in the Bronze Age. There is no obvious evidence of copper smelting in this area, perhaps because of the intensive exploitation of lead and silver in later periods (mainly in the 1st millennium BC and in the 19th – 20th centuries), however, rich copper ores in Lavrion still can be found and the lead isotope evidence is compelling (Stos-Gale et al. 1999).

It is quite interesting to look at all these mining regions mentioned above on the map. All of them are either coastal (Lavrion, some Cypriot mines), or have a very easy access to the sea. It is quite clear that the major metal trading routes would be criss-crossing the Mediterranean. In the Aegean and in Cyprus the major LBA sites are also near the coast. Could one then expect perhaps that ships like the Gelidonya, carrying ingots and scrap metal, would carry a selection of metals used in the whole region?

Metal cargo of the Cape Gelidonya shipwreck and its origin

Cape Gelidonya is the Chelidonyan Promontory of Pliny's *Natural History* in Lycia. On modern maps of Turkey this is the cape marking the western extremity of the Bay of Antalya. In about 1200 BC a merchant ship ripped its bottom open on the rocks just under the surface of the water, spilling artefacts in a line as

it sunk. The main part of the cargo rested at a depth of about 28 m and was discovered in 1954 by local sponge divers who described it to the American journalist and amateur archaeologist Peter Throckmorton. The sponge divers described the oxhide ingots (see for example: Gale 1991) as objects shaped like 'biscuits with ears' (G. Bass, personal communication). The oxhide ingots are Bonze Age artefacts of a unique type, the shape used only in the Late Bronze Age Mediterranean for pure copper and tin. Small numbers of these artefacts were found on Crete, Mainland Greece, Bulgaria, Egypt, Turkey and Sardinia, but by weight all of them together form only a small fraction of those from the Gelidonya and Uluburun shipwrecks. Many articles have been devoted to the phenomena of the 'oxhide ingots', objects also regarded by some as a primary form of currency (for references see: Stos-Gale et al. 1997). The majority of finds of these ingots is dated to the 13th–12th c. BC, the sole exceptions are ingots from Ayia Triadha (LMIB) and Mochlos (LMII) on Crete that belong to the 15th c. BC or earlier, and the Uluburun ingots. It has been suggested long ago that these ingots were cast directly from smelted copper (Stech Wheeler et al. 1975) and it seems that there is no further evidence negating this conclusion.

The excavation of the Gelidonya site in the 1960s was the first underwater shipwreck excavation conducted following the standards of terrestrial archaeological excavation. The sinking of the ship was dated to 1200 BC ±50 years by radiocarbon from brushwood on the wreck. Intact Mycenean IIIB stirrup jars found on the site fully corroborated this date (Bass 1967). Most of the cargo consisted of ingots of copper and tin, including 34 whole copper oxhide ingots (weighing about 25 kg each) and their numerous fragments, over 30 'bun' ingots and their fragments (a few kg of copper each) and 18 small ingots cast in multiples of 0.5 kg. The tin ingots were too badly corroded to reveal their actual shapes and numbers. The finds of many roughly cast and broken bronze tools, the bronze swage, stone hammers and many stone polishers and a whetstone and an anvil suggested that the ship carried a travelling tinker. At the time of excavation it was generally accepted that Mycenenan Greeks had a monopoly on maritime commerce in the eastern Mediterranean in the LBA. The pottery excavated on the site was a mixture of Mycenenan, Cypriot and Syrian. The private possession of the crew included four scarabs and a scarab shaped plaque, Syrian stone mortar, a Canaanite lamp and a Syrian merchant's cylinder seal. Also the set of stone balance weights was generally Near Eastern, not Mycenean. On the grounds of these finds George Bass concluded that the crew of the ship was of Near Eastern rather than Cypriot or Mycenean origin (Bass 1991), even if all the metal cargo was accepted as coming from Cyprus.

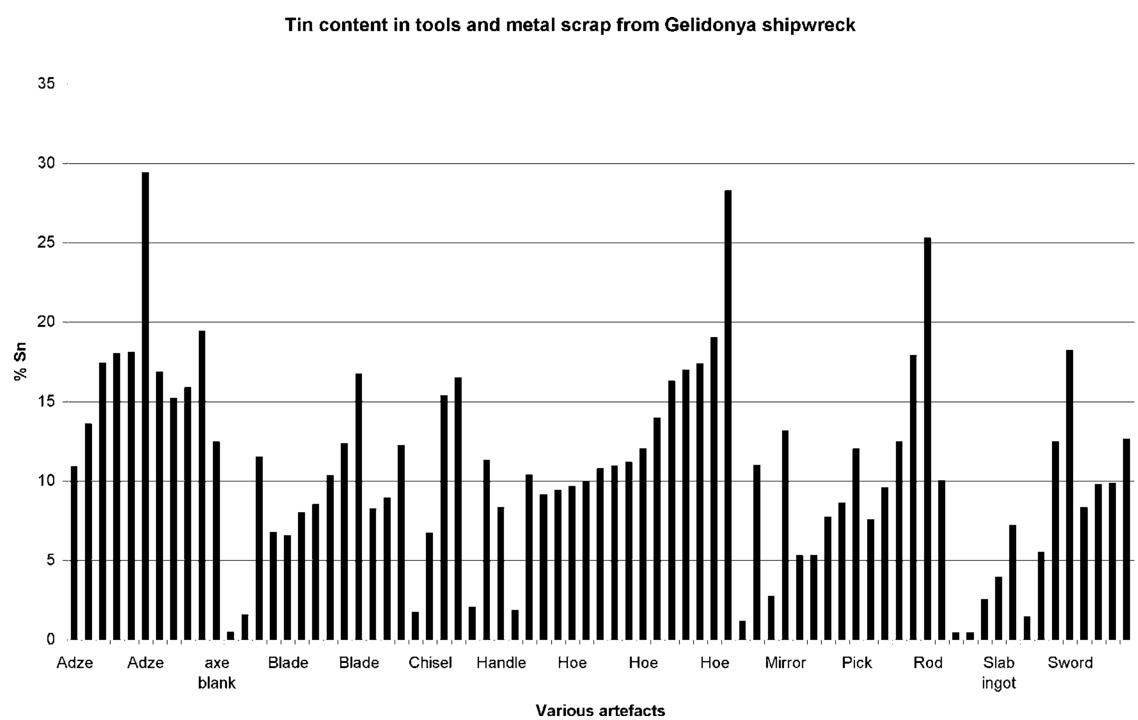


Figure 1: Tin content in tools and metal scrap from the Cape Gelidonya.

Together with Noel Gale we were able in 1995 to take samples of 202 copper-based metals from the Gelidonya. This number includes 82 oxhide ingots and fragments, 31 bun ingots, 5 slab ingots, 2 swords, 51 tools and other 31 assorted metal fragments. Out of this group 30 oxhide ingots and 9 other metal fragments were analysed in the Isotrace Laboratory for their major and trace elemental composition using neutron activation analysis (for details of the method see Stos-Gale 1991). The alloy compositions of all the remaining artefacts were checked by the author using semi-quantitative ED XRF analysis in the Research Laboratory for Archaeology and the History of Art. Additionally, 5 bronze weights brought to Oxford by Cemal Pulak were also non-destructively tested. The full report on the results of this work will be published as a collaborative archaeological and scientific report including input from all collaborators.

The ED XRF analyses of the drilled samples of metal tools and scrap show that the tin content in all these objects is very varied, but many of them contain tin in excess of 10%, that is much more tin than is usually found in the Mediterranean LBA tools (data from the Isotrace Laboratory plotted in Figure 1). The Gelidonya ship carried copper and tin ingots, but it is also possible that some of the very high tin roughly cast tools (many hoes are not finished) could have been melted together with small fragments of copper ingots to make a new tool with a smaller amount of precious tin. How such activity would influence the lead isotope data?

The lead isotope analyses of metal tools and scrap from Gelidonya are listed in Table 3 (see appendix) together with an indication of their origin according to the comparisons of LI ratios for ore samples from all deposits listed above. At first the comparisons were made with all available LI data for ores and slags using simple software (TestEuclid) that calculates the Euclidian distance (TED) between the points in three-dimensional space. The overall accuracy of the TIMS lead isotope analyses is ±0.1% of each LI ratio, the TED is expressed as the fraction of this error. That means that two points at *TED = 1* are identical within 1 analytical error and therefore the metal and the ore/slag can have the same geological origin.

Usually these comparisons produce a number of ore specimens numerically identical to the artefact. For identification of the source of copper-based metals only ores from deposits that contain copper ore must be included. The next stage of identification of the source relies on the 2D plots of the data points to check the grouping. Figure 2 shows the LI plots of the main group of these artefacts and copper ingots compared with ores and slags from Cyprus.

The results of melting together pieces of metal of different LI composition are presented graphically on Figure 2: if a group of high tin artefacts marked A was mixed with fragments of copper ingots B, then the resulting artefacts would have to lie on the line joining the points A and B, for example they could be the groups of artefacts represented by points C1 and C2.

Looking in more detail at the impact of mixing together copper from different sources on the lead isotope data, the lead content in the copper from different sources and the respective amount of metal from each source that has been used has to be taken into account.

Table 4 shows two examples of calculations using lead isotope compositions of metals from the BA Eastern Mediterranean (Timna, Cyprus, Lavrion and Trabzon in Turkey on the Black Sea coast) using different quantities of metal with varying lead content. Lead in small quantities (usually below 1%) is quite common in copper ores, but tin ores usually contain no more than a few parts per million (1 ppm = 0.0001%) of lead, so lead from tin will have no influence on the lead isotope ratios resulting from the mixing.

In this example, because of the amount of copper A1 from Lavrion used for adding to the B1 tin-bronze

Table 4: Examples of calculations of lead isotope ratios of metal C made by melting together metals A and B.

	Metal A (Cyprus)	**Metal B (Timna)**	**Resulting Metal C**	**Metal A1 (Lavrion)**	**Metal B1 (Trabzon)**	**Resulting Metal C1**
Mass	500g	100g	600g	500g	100g	600g
Lead content	0.1%	0.05%	0.09%	0.1%	0.05%	0.09%
Tin content	0.001%	10%	1.7%	0.001%	10%	1.7%
$^{208}Pb/^{206}Pb$	*2.07500*	*2.1200*	*2.07902*	*2.05970*	*2.08840*	*2.06228*
$^{207}Pb/^{206}Pb$	*0.84100*	*0.8670*	*0.84332*	*0.83141*	*0.84620*	*0.83274*
$^{206}Pb/^{204}Pb$	*18.550*	*17.890*	*18.489*	*18.868*	*18.430*	*18.828*

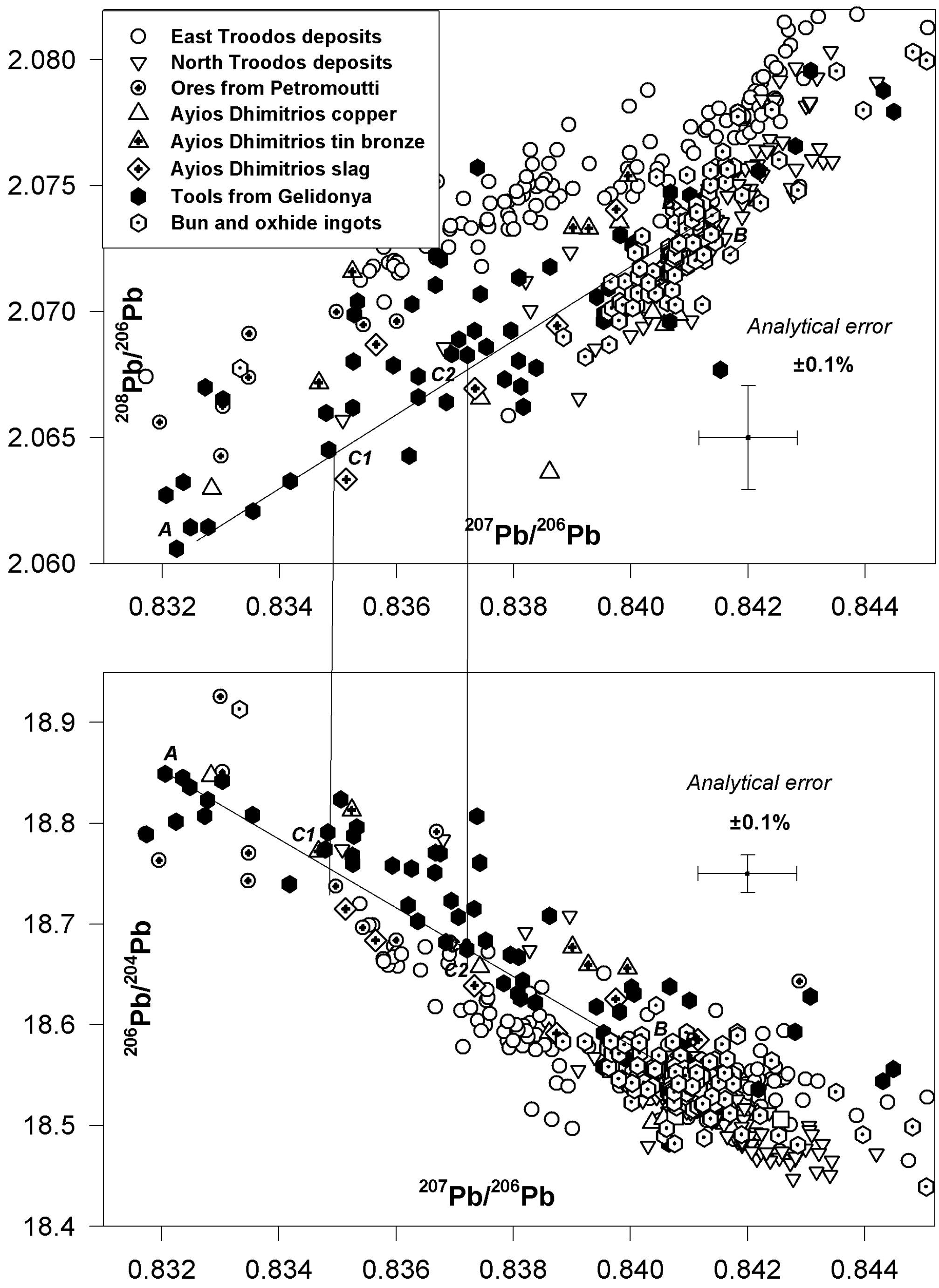


*Figure 2: Cypriot ores and metallurgical finds from Ayios Dhimitrios-Kalavasos and metal finds from the Cape Gelidonya and Late Bronze Age shipwrecks off the coast of Israel. Principle of mixing: Groups of tools **C1** and **C2** could have been made by melting together fragmens of ingots **A** and **B**.*

from Trabzon and the higher concentration of lead in copper from Lavrion, the lead isotope composition of the resulting low-tin bronze will be also consistent with Lavrion. This case can be regarded as typical for possible production of low-tin bronzes in the Aegean. Since it is most likely that local copper was used for 'dilutions' of high tin bronzes, then the lead isotope compositions of thus prepared low tin bronzes would still indicate local origin of copper. Therefore, in the interpretation of the lead isotope data the simplest answer is used: for example on Figure 2, metals C1 and C2 might have been made by adding Lavrion copper (point A) to Cypriot, but the amount of Cypriot copper must have been greater than Lavrion (Cypriot ores are very low in lead), so these artefacts will be indicated as of Cypriot copper.

Discussion of the groups of metal objects from the Gelidonya shipwreck

Fragments of metal

Thirty fragments of metal of various descriptions were analysed. They included: seven rods, three bars, one fragment of thick copper sheet, one oval lump (casting waste?), one metal strip/bar, four fragments of tools, a fragment of a mirror, and 12 shapeless lumps of copper. Out of this last group 11 pieces (GEL 8, 8/85, 4/89,35,4/95,17, 1 11 3 24, 25a and 25b) are almost certainly pieces of ingots. The XRF analysis shows that all of them are pure copper with quite high contents of iron (most likely in the form of iron oxides), which is characteristic of unrefined copper. All these fragments are consistent with LI compositions of ores from the Cypriot mines, mostly from the Solea region (Apliki, Skouriotissa, Phoenix and Konizi), but also from the Limni region and one fragment is consistent with ores from the Mitsero region, south of Nicosia. Also the copper sheet (GEL 84) contains high iron (1.6%) and possibly is from an ingot; it is also made of Cypriot copper. A shapeless piece (GEL 4/89) contains about 1.6% of tin and is consistent with the ores from the Kamaresa mine in the Lavrion district in Attica. The same origin is indicated by the LI ratios of a metal strip or bar B224 (218/BW W98) that contains 5.5% of tin. Another two fragments of tools (B095 and B283) with high tin contents (9.8% and 8% respectively) are also fully consistent with the origin of copper from Lavrion. Another oval piece, possibly casting waste (B236) also contains 1.7% of tin and its LI composition is close to ores and slags from the Cypriot site of Petromoutti, north of Limassol.

Three metal bars are very different isotopically. A bar fragment B21 (280/BW G54 236) was paralleled by Bass in 1967 (86, Fig. 100) to a similar object from Cyprus, contains 6.7% of tin and indeed is isotopically identical with copper ores from the Skouriotissa mine. Another bar (290/W 9 13) contains 11.5% of tin and has LI ratios identical with copper slag from Ayios Dhimitrios, a LBA site on the coast near Limassol. Possibly it is a piece of metal made there from Cypriot ores from various mines. The third bar with rectangular section B223 (214/BW P52 49) contains only a small amount of tin (about 0.5%) and is fully consistent with copper from Sardinian mines either of Salondra or Funtana Raminosa.

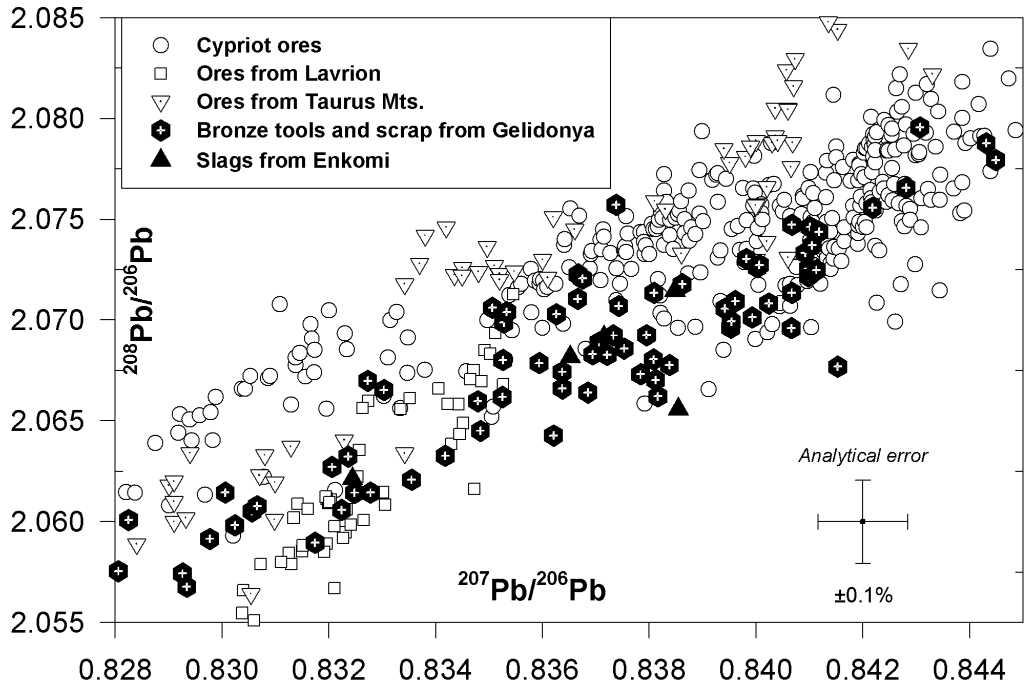
The seven rods are a very interesting group of artefacts. Six of them are made of a very good quality tin-bronze and they would provide a very good source of metal for casting small, narrow tools or weapons. They are all made of copper isotopically consistent with the copper deposits in north Troodos (Apliki, Skouriotissa, Phoenix). The mirror fragment (227/GW1) contains 13% of tin and is fully consistent with the ores from the Phoenix mine in the Solea region of Cyprus. And finally, two fragments of tools (B045 and B281) containing 9.8% and 12.6% of tin respectively have lead isotope compositions resembling closely the ores from the Bolkardag range in the Taurus Mountains.

The bun and oxhide ingots (LI data not included in this paper)

Thirty of the bun ingots are made of pure copper and show remarkably uniform Cypriot origin. The majority of them is fully consistent with the LI ratios of the copper ores from the Solea region (Apliki, Phoenix, Skouriotissa, Konizi), but four are from the Limni mines and one (BI95/8) is consistent with a slag collected in the region of the archaeological excavation at Phorades.

An exception amongst the samples of bun ingots is one quarter of a bun which is isotopically quite different to the other bun ingots and again is consistent with ores from the Bolkardag range in the Taurus Mountains. However, this artefact is altogether different from other bun ingots, because it is not unrefined copper, but an alloy of tin and copper, containing 12.2% tin, a perfect proportion for bronze casting.

All oxhide ingots from the Gelidonya are consistent with origin from Cypriot ores. It is quite possible also that all of them originate from copper mined in the Solea region of Cyprus (Stos-Gale et al. 1998a). Even if the closest TE distance for some of them is for ore samples from Limni or Mitsero, always, the next closest (and well within the analytical



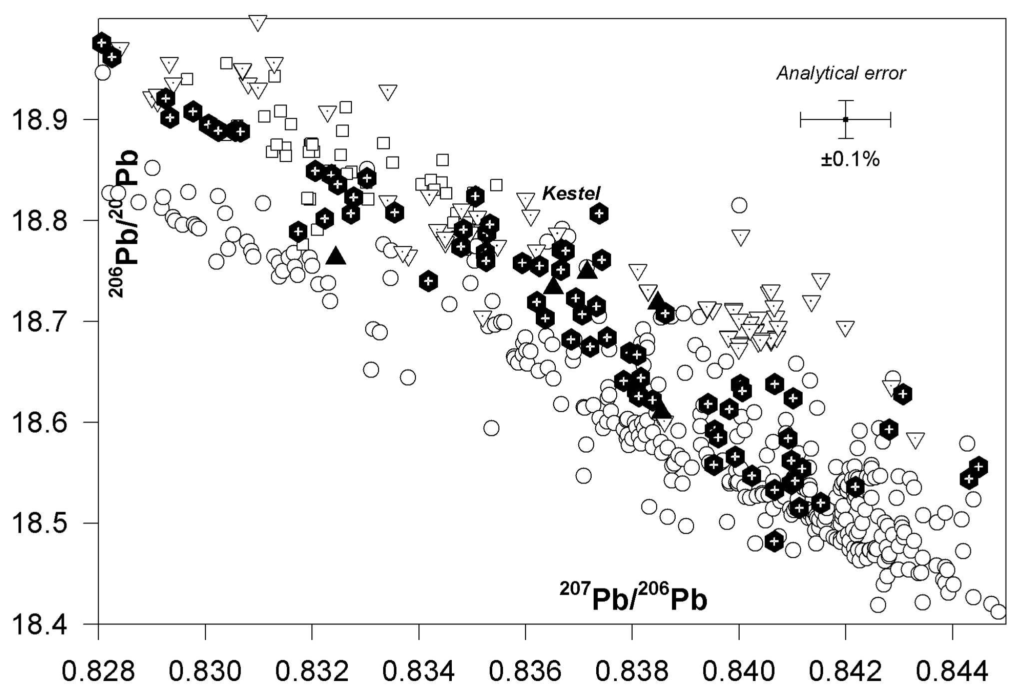


Figure 3: Lead isotope compositions of the bronze tools and scrap from the Cape Gelidonya shipwreck compared with ores from Greece, Cyprus and South Turkey.

error) is an ore from the Solea mines (Apliki, Skouriotissa, Phoenix and Mavrovouni are within a few kilometres from each other).

Remarkably also, some of the Gelidonya oxhide ingots are isotopically identical with ingots from Enkomi and pieces of metal and slag from the site of Ayios Dhimitrios-Kalavassos.

The slab ingots

This description was given in 1967 to a group of rather small flat and elongated pieces of metal weighing around 1 kg. We had six samples of these ingots (out of 19 listed in Bass 1967, p. 82). All these ingots contain low quantities of tin, ranging from 0.4% to 3.9%. In one of them (SI9) the tin was measured at 7.2%. Five out of six of these ingots are fully consistent with the copper ores from Lavrion, one is Cypriot, possibly from the area of Phorades, or Limassol.

The tools and weapons

We have analysed for their lead isotope composition 51 tools including seven adzes, six axes, five chisels, 20 hoes, two knives, one mattock, four picks, one nail and two swords (B264 and B267). In this group there are also included three samples of tripod handles (B177a&b and B280). All of the tools analysed for their alloy composition contain varying quantities of tin.

The variety of metal origin in this group is quite remarkable and these results require much more discussion including an input from the excavator (G. Bass). Figure 3 represents the LI plot of the data for the major group of these objects compared with the data points for ores from Cyprus, Lavrion and the Taurus mountains; the identification of sources for each of the artefacts is listed in Table 3. One interesting object is the sword B264 that is consistent with copper ores from the Taurus. Could it be a Hittite weapon?

Figure 4 shows a chart representing the fractions of metal of different origin present in the cargo, excluding the copper ingots. The lead isotope analyses indicate that the cargo of copper on the Gelidonya ship was predominantly originating from Cyprus (if the ingots are included than it is over 75%, rather than 59%). However, in particular amongst the tools, small ingots and small fragments of metal there are many other sources of metal represented. Lavrion was a predominant metal source for the Minoans and Myceneans (who also used a reasonable amount of Cypriot copper). Copper from the territories under the Hittite influence, Taurus and Timna, also found its way into Gelidonya's metal assemblage. A few pieces of metal of Sardinian origin perhaps are also not so suprising, since on Sardinia Cypriot pottery and copper metal from Cyprus was found. Also Sardinian silver and lead were found in Cyprus and Ugarit, and in some LBA Near Eastern hoards.

The origin of metal cargo of the Uluburun shipwreck

The ship that sunk around 1307 BC off the south-west coast of Turkey near the Great Cape (Uluburun) was about 15 m long and carried a cargo of nearly 20 tons (Bass 1987; Pulak 1998). Ten tons of that cargo consisted of raw copper in the shape of ingots, including 354 of 'oxhide' shaped large ingots weighing on average 24 kg each (31 of them are unique two-handled ingots) and 150 small 'bun' ingots weighing on average 6.2 kg, and their fragments. Other raw materials of the cargo included tin and glass ingots, ebony logs, ivory and terebinth resin. The finished items consisted of large quantities of Cypriot pottery, glass and faience beads, faience drinking cups and copper vessels. Almost all of the artefacts on the ship might have been acquired at a Cypriot or Syro-Palestinian port. The details of the excavation and the artefacts are currently on display in a special exhibition in the Bodrum Castle in south-west Turkey. The origin of copper ingots carried on this ship was of particular interest, because they are the first and only find of such large number of oxhide and bun ingots found together in a well dated late 14th c. BC context.

Preliminary lead isotope analyses of 60 oxhide ingots from the Uluburun (this shipwreck has been also known as the Kaş wreck, from the name of the nearest town) indicated that the source of copper ore used for their production was most probably on Cyprus, but the minerals were geologically different from those used for all the other, mostly later, 'oxhide' shaped copper ingots (Stos-Gale et al. 1998a and 1997). Now we have analysed all 'bun' and the majority of 'oxhide' copper ingots and the conclusions remain basically the same: all these ingots form essentially a coherent isotopic group, indicating that the overwhelming majority of the metal was derived from a geologically uniform deposit, most probably located on the island of Cyprus. There is no difference in the lead isotope compositions of the 'oxhide' and 'bun' groups.

A fully collaborative publication of the metal finds from the Uluburun shipwreck is in preparation. Further analyses of the ingots, nearly 300 have been analysed by now, not only in the Isotrace Laboratory, but also in three other laboratories using MC-ICPMS, confirmed that all of them are of pure copper and all

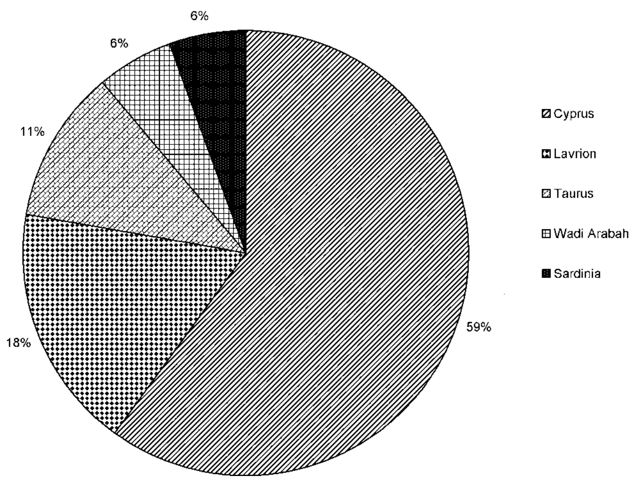


Figure 4: Origin of copper based tools and metal scrap from the Gelidonya shipwreck without ingots.

are consistent with the origin from Cypriot ores from different parts of the island.

We have also analysed in the Isotrace Laboratory over 30 bronze tools from the Uluburun. Their lead isotope pattern is very different from the metals carried on Gelidonya: the majority of the bronzes are not made of Cypriot copper; they are consistent with the ores from south-east Turkey. Only a sword and two spearheads are consistent with an origin from Cypriot ores, and a few tools might have been made from Lavrion copper.

The lead isotope evidence confirms the difference between the cargoes of these two Bronze Age ships: whilst the Uluburun indeed was loaded with valuable raw materials and personal possessions of the rich, the Gelidonya carried metals needed for making tools and weapons necessary in daily life of Bronze Age people and representing metal originating from the regional copper mines and some brought to the eastern Mediterranean from Sardinia and perhaps just circulating there. One of these ships could have been indeed carrying a king's gifts, the other was just a sailing smithy.

The origin of copper used on Crete in the Late Bronze Age

Production of metal objects, from copper and bronze weapons to gold jewellery, was very well developed on Crete since the EBA (Branigan 1974). It seems that most of these activities in the LM period was taking place in settlements and in the vicinity of the palaces, as proven by workshops in Zakros, Malia and Knossos (Evely 2000). The Linear B tablets excavated in the palaces indicate that records of metal supplies and distribution were diligently kept. However, raw copper metal was also worked at the port of Kommos in the Neopalatial and LM IIIA1–B period, in the town of Gournia and in the harbour of Poros. But the largest number of pieces of copper ingots have been found in workshops of the recently excavated LMIb settlement in the village of Mochlos on the north-east coast of Crete. There is no evidence of any kind (including lead isotope analyses and geological surveys) that small occurrences of copper and lead that still can be found on this island have been used in the Late Minoan period. It is therefore certain that all metal must have been brought to Crete on ships.

Out of a large number of metal finds from the LMI workshops in Mochlos (Soles and Davaras 1996) 87 fragments of copper have been sampled with the kind permission of the excavator and the East Crete Archaeological Service. The group consisted largely of fragments of pure copper ingots with large gas holes, some of them were clearly fragments of oxhide and bun ingots (49 pieces). Others represented shapeless lumps of metal, spills of melted copper and thin discs and strips. These metals are about 300 years older than those from Gelidonya, but the visual characteristics of the ingot metal are identical with all other oxhide ingots sampled so far (see Stos-Gale et al. 1997): the ingot fragments are very porous and with a 'fleecy' appearance on the top surface due to large gas bubbles, and spongy looking but smooth bottom.

The majority of these copper fragments, including all ingot pieces, is consistent with an origin from Cypriot ores (Fig. 5). Many other small metal fragments and the metal strips are consistent with copper ores from Lavrion in Attica and from the Taurus Mountains in southern Turkey. The excavation reports from Mochlos are being currently prepared (Soles et al. 2004) and only when the complete archaeological evidence is available it would be possible to attempt the interpretation of the metallurgical significance of this settlement, but on the basis of the lead isotope evidence available at present the conclusion points to a presence in Mochlos of a cargo of a ship that brought copper ingots and perhaps also bronze scrap from the eastern corner of the Mediterranean, Cyprus and the southern coast of Turkey. The mines of Bolkardag are just north of the port of Mersin.

This pattern of metal origin is not at all reflected amongst the 139 MM–LMI and 161 LMII–LMIII

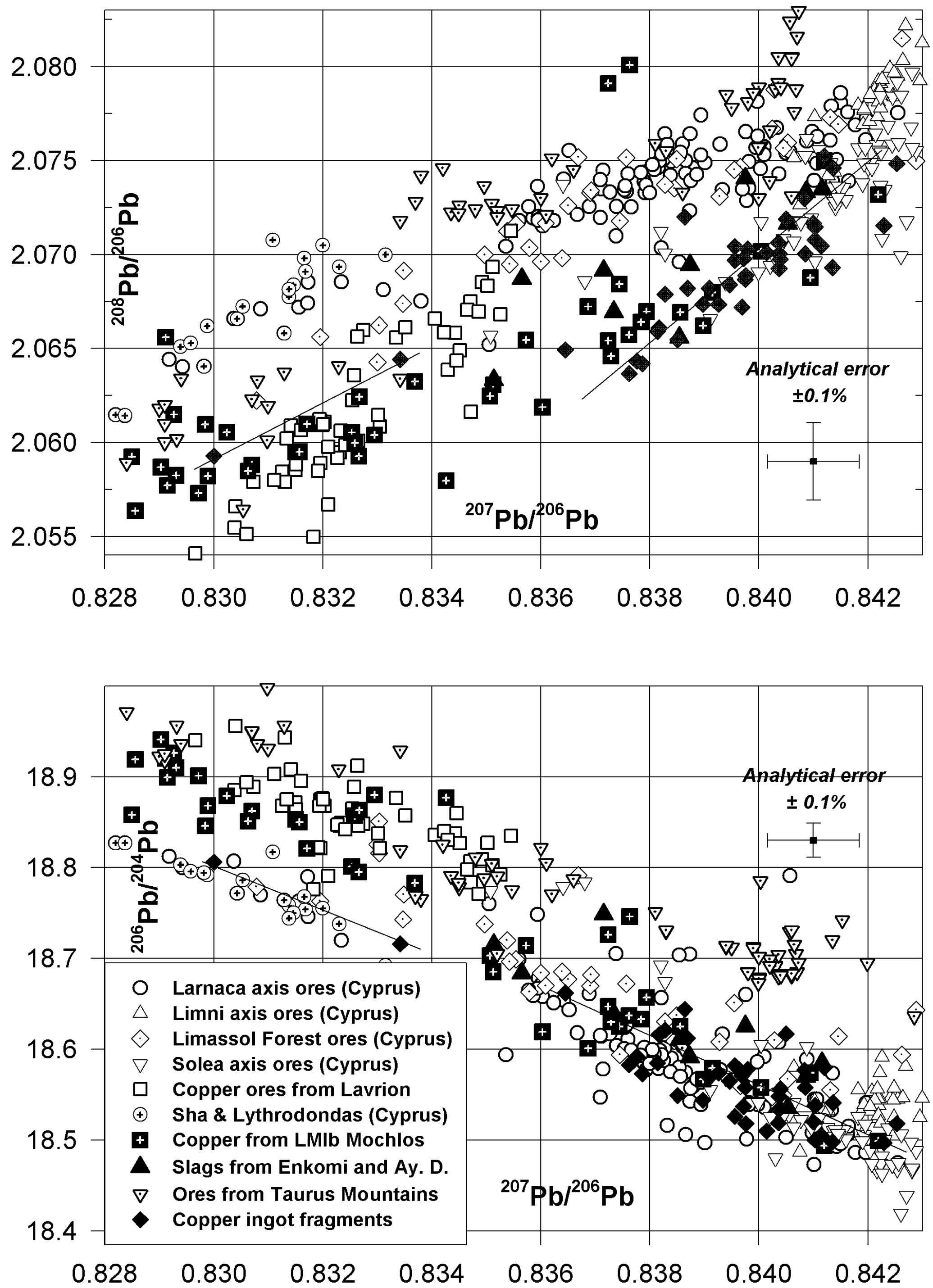
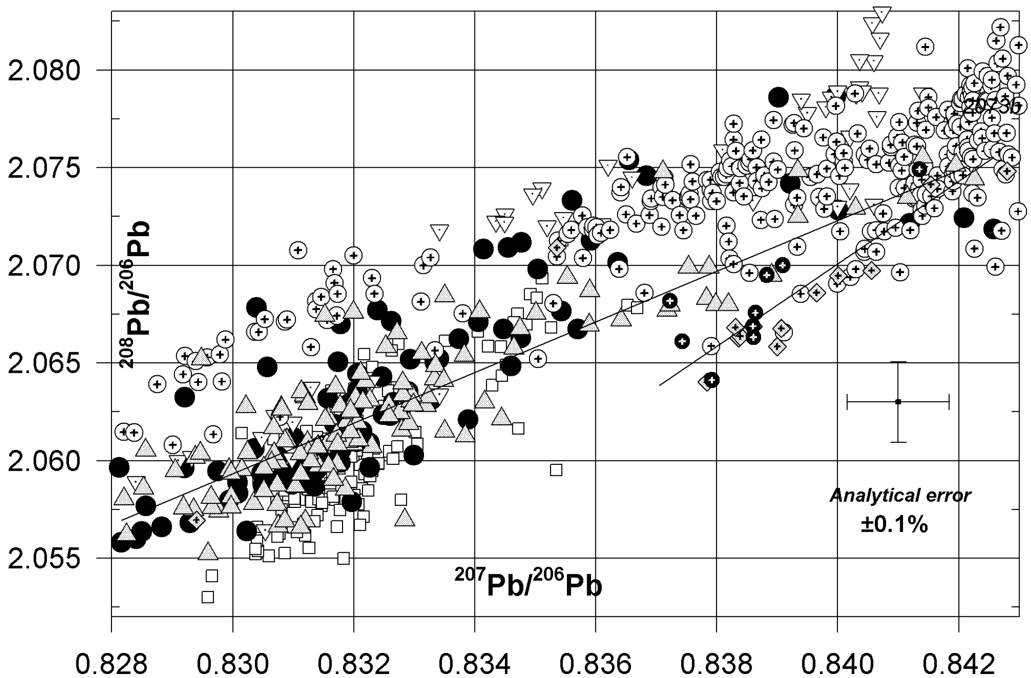


Figure 5: LI compositions of metals from LMI Mochlos, ores from Lavrion, Bolkardag and Cypriot ores and slags.



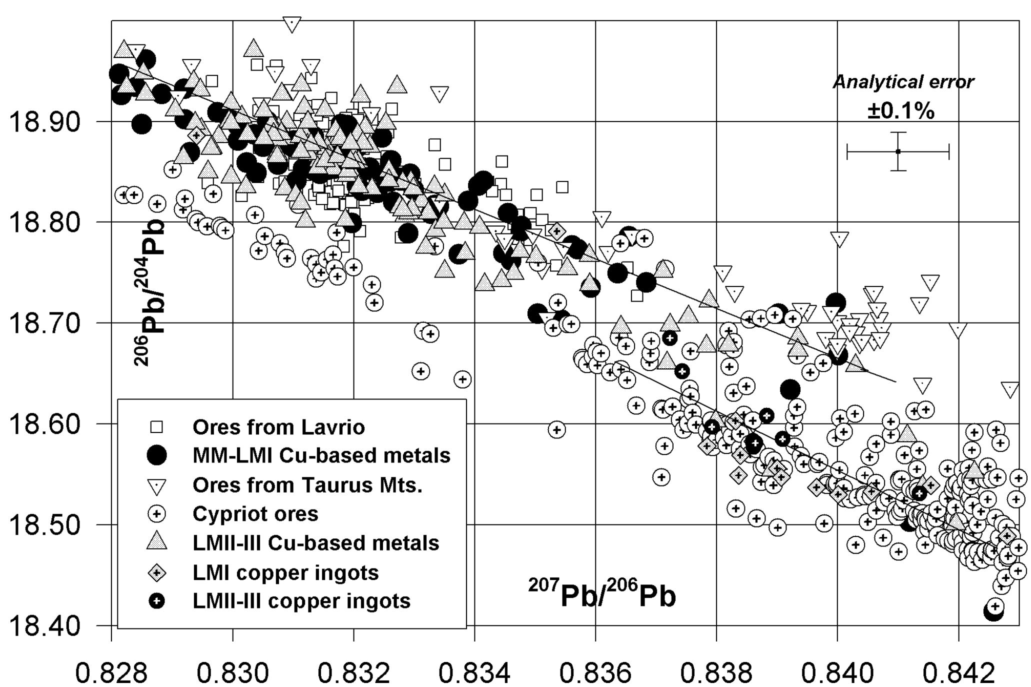


Figure 6: LI compositions of Minoan Copper-based metals. The large group of oxhide ingots from Ayia Triadha is considerably out of the LI range of this graph.

copper-based Cretan metal objects analysed in the Isotrace Laboratory. In fact nearly 50% of the copper excavated on various sites across Crete, including Knossos, Phaestos and Palaikastro, is consistent with an origin from the Lavrion ores (Fig. 6). We have analysed in the Isotrace Laboratory 240 Late Minoan copper based artefacts for their elemental composition (using ED XRF or NAA): this group included tools, weapons, vessels and small items like beads and tacks. Out of this group 196 objects, that is nearly 82%, contain added tin, in 170 of them the tin content is above 2%. The objects that do not contain tin are mostly vessels, double axes, small items and a few figurines. This simple statistic shows clearly that tin was an essential raw material for the Late Minoan smith.

Therefore the ships that brought copper ingots to Crete must have also been bringing tin ingots, as witnessed by the finds from the Gelidonya and Uluburun.

It has been a puzzle for us to see from the lead isotope analyses of copper artefacts from the Bronze Age Aegean that whilst the great majority of pure copper ingots and their fragments from Crete, Kea and Mycenae (Poros Wall Hoard) are consistent with their origin from Cyprus, the bronze artefacts are predominantly consistent with an origin from Lavrion mines. Another puzzle are the LMI (15th c. BC) oxhide ingots found in the store-rooms of the palace of Ayia Triadha (Gale and Stos-Gale 1986; Gale 1991). These ingots can be regarded as the prototypes of what from the 13th century seems to be the shape only used for the copper extracted from Cypriot ores. They show lead isotope compositions that so far have not been identified amongst any copper ores in the Mediterranean and could not have been obtained by mixing ores from several Mediterranean ore deposits ($^{208}Pb/^{206}Pb>11$). They represent nearly 300 kg of copper, perhaps a gift from a king? However, amongst the LMI artefacts excavated on Crete this LI composition is practically non-existent. Perhaps the king offered copper to the Minoan ruler, but did not supply tin ingots to make this copper useful?

A similar situation is apparent in Figure 6: the majority of the ingots from Cyprus is consistent with an origin from the Apliki and Skouriotissa mines, but the bronze artefacts are identical as a group with the group representing copper ores from Lavrion and Cypriot mines not located in the Solea Valley. Ingot fragments from Mochlos are not plotted on Figure 6 for the sake of clarity of the diagram, but as seen on Figure 5, these fragments of pure copper also are mostly identical isotopically with the ores from the Solea Valley in north east Cyprus.

Conclusions

The space in this *Festschrift* is limited and therefore only limited evidence from our 25 years of research into the sources of metals in the Bronze Age Mediterranean can be presented here. Also, in spite of the many years of work in the laboratory and numerous archaeometallurgical surveys in the relevant countries, we realise that all the information obtained in Oxford and in other research institutions that have been involved in similar research (above all Mainz, Heidelberg and Freiberg) is only a tip of an iceberg. We have analysed only a fraction of the excavated Bronze Age metals from this area, and that is only a fraction of what was circulating there 4 or 3 thousand years ago. However, we can regard our sample as statistically valid, selected without any prejudice, and perhaps we can try to assess the picture related to the influx of Cypriot copper into the Aegean.

First, the question of the methods used for distributing Cypriot copper: two shipwrecks that have sunk in not a great distance from Cyprus represent two different modes of copper transport. The cargo of the Uluburun has all features of a tribute of one ruler to another, or a ship furnished by a rich trading community. The cargo of Gelidonya represents an assembly of a small merchant ship. The fragments of copper ingots in the workshops of LMIb Mochlos could have very well been brought by such a ship. If the cargo included also tin ingots or bronze casts of tools these would have been made into finished tools and weapons and sold; the pieces of copper ingots might represent the surplus of copper over tin. Similar Cypriot ingot fragments have been identified in many other LM sites, for example in Knossos, Palaikastro, Gournia, Kato Simi, Zakros (whole oxhide ingots) and Chania.

The second question: if there were so many ingots of Cypriot copper reaching Crete, why the majority of the LM Cretan artefacts does not show the same LI composition? We really cannot blame the addition of tin for the change of LI composition because the metals falling with the Lavrion ores have tin content between 0.1 and 20%. If the shift was influenced by tin, then it would also reflect the tin content. Therefore, we have Cypriot copper ingots and bronzes made of copper from Lavrion. Why this discrepancy?

There could be perhaps more answers than one to this question. However, it seems highly probable that we can see here some lack of co-ordination on the part of the merchants distributing Cypriot copper in supplying the correct amount of tin with it. Cemal Pulak, the excavator of Uluburun, has remarked that the proportion of tin to copper ingots on this ship was just right for making bronze (10:2). Perhaps the

small tinker-sailors could not afford enough tin to match the quantity of much cheaper Cypriot copper that was flooding the market and topped their cargoes up with the bronze scrap that contained copper from other mining regions: on the Gelidonya it was Lavrion, Wadi Arabah, Taurus and Sardinia. In the Aegean the scrap would be mostly containing copper from Lavrion that was locally available since the Early Bronze Age and widely used.

We can suggest also another scenario: if for example the Minoan palaces were controlling the supply of copper from Lavrion and tin coming with it (we still do not know where from, unfortunately) they were able to distribute to the workshops on the island material for bronze. If in parallel the coastal settlements have been also visited by small tinker-sailor ships bringing metal circulating in the south eastern Mediterranean, where Cypriot copper was dominating, then Cypriot copper would become cheaper and more plentiful, but without the matching amount of tin it would be of little use.

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Notes

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Table 3: Lead isotope ratios of copper-based artefacts from Cape Gelidonya shipwreck

Number	Bass 1967	Description	208Pb/206Pb	207Pb/206Pb	206Pb/204Pb	Origin
217/BW S 150/**B107**	p.95, Fig.109&110	Adze, lugged	2.07106	0.83666	18.751	Cyprus
221/BW S 26/**B220**	p.113, Fig. 126&127	Hoe, small flat blank	2.06743	0.83637	18.361	Cyprus
292a/BWPII 131/**B055**	p. 88, Fig.102&105	Hoe with cube of metal, blank	2.07013	0.83993	18.566	Cyprus, Apliki
GEL 25a	not published	Metal lump	2.06962	0.83953	18.558	Cyprus, Apliki
GEL 35	not published	Metal frag., flat	2.07248	0.84113	18.515	Cyprus, Apliki
GEL 4/95	not published	Metal frag., lump	2.07083	0.84024	18.547	Cyprus, Apliki
GEL 8	not published	Metal frag.	2.06769	0.84153	18.520	Cyprus, Apliki
GEL 8/85	not published	Metal frag.	2.06960	0.84066	18.482	Cyprus, Apliki
W9-2829	not published	Rod, cylindrical section	2.07136	0.84067	18.533	Cyprus, Apliki
225/BW W9 11/**B130**	p.100, Fig. 112&113	Chisel, narrow	2.06828	0.83721	18.675	Cyprus, Ay. Dhimitriios
232/BW S20 137/**B097**	p.94, Fig. 107&108	Mattock	2.06890	0.83706	18.707	Cyprus, Ay. Dhimitriios
290/W 9 13	not published	Bar of metal	2.06641	0.83685	18.682	Cyprus, Ay. Dhimitriios
294/PII 25	not published	hoe	2.06860	0.83753	18.684	Cyprus, Ay. Dhimitriios
305/BW EII 444/**B053**	p. 88, Fig.102	Hoe blade	2.06428	0.83621	18.719	Cyprus, Ay. Dhimitriios
309/BW G42 285/**B058**	p. 88, Fig. 102	Hoe, flat blank, type 2, rounded end	2.06787	0.83594	18.758	Cyprus, Ay. Dhimitriios
358/95 box 2	not published	Hoe, completely encrusted	2.06661	0.83637	18.703	Cyprus, Ay. Dhimitriios
B254	p.117	Rod or tool frgm., triangular section, 0.44 m long	2.08238	0.84813	18.436	Cyprus, Ay. Dhimitriios
B275	not published	Hoe, small	2.06327	0.83418	18.740	Cyprus, Ay. Dhimitriios
B277	not published	Rod	2.07030	0.83626	18.755	Cyprus, Ay. Dhimitriios
B282	not published	chisel, small	2.06831	0.83694	18.723	Cyprus, Ay. Dhimitriios
BWG 50 24(B)	not published	Rod fragment, cylindrical	2.06924	0.83733	18.715	Cyprus, Ay. Dhimitriios
257/BW C140 344/**B005**	p.86, Fig. 99&101	Pick	2.06731	0.83784	18.641	Cyprus, Ay. Dhimitrios
270/BW P56 52/**B053**	p.88, Fig 102	Hoe, Type 1	2.06622	0.83816	18.644	Cyprus, Ay. Dhimitrios
295/BW W96 (?)/**B048**	p.88, Fig 102&105	Hoe, Type 1	2.06805	0.83808	18.631	Cyprus, Ay. Dhimitrios
BWG 417	not published	Hoe Fragment	2.06703	0.83812	18.626	Cyprus, Ay. Dhimitrios
B262	not published	Hoe, small	2.06777	0.83838	18.622	Cyprus, Ay. Eftychios
GEL 25b	not published	Metal lump, flat	2.07256	0.84098	18.539	Cyprus, Konizi
275/BW C35 140	not published	Knife blade	2.08165	0.84730	18.431	Cyprus, Limni
298/BW ?9 9/**B103**	p.95&96&94, Fig.107&108	Axe half (similar found at Enkomi)	2.07657	0.84281	18.593	Cyprus, Limni
GEL 1	not published	Metal frag., lump	2.07438	0.84118	18.554	Cyprus, Limni
GEL 17	not published	Metal frag., lump	2.07558	0.84218	18.536	Cyprus, Limni
GEL 84	not published	Sheet, thick	2.07371	0.84105	18.542	Cyprus, Limni
220/BW P51 50/**B212**	p.112, p.111 'tang',Fig.122&123	Chisel, unfinished cast	2.07070	0.83743	18.761	Cyprus, Mavrovouni
262b/BW ?/**B177**	p.107, Fig. 116&117	Handle fragment or part of a tripod	2.07273	0.84006	18.631	Cyprus, Mitsero
342/95	not published	Chisel fragment, tip	2.07261	0.84002	18.637	Cyprus, Mitsero
GEL 11	not published	Metal frag., lump	2.07304	0.83982	18.613	Cyprus, Mitsero
222/BW EI 444/**B105**	p.95, Fig.109&110	Adze, plain	2.07794	0.84449	18.556	Cyprus, Petromoutti
307/W 9 25 box 2	not published	Axe blank, or bar	2.07878	0.84431	18.544	Cyprus, Petromoutti
B236	p.116, Fig. 127	Casting waste, oval lump, s. 14.12.90	2.07572	0.83738	18.807	Cyprus, Petromoutti
SI 18	p.82, Fig. 96	Slab ingot, L. 0.085, W.0.068, Th. 0.01. 0.3kg	2.07473	0.84067	18.638	Cyprus, Petromoutti
227/GW1 box 2	not published	Mirror frgm	2.06925	0.83795	18.669	Cyprus, Phoenix
235/BW 93 77/**B108**	p.97&98, Fig.109&110	Adze blade, flat axe	2.06451	0.83484	18.791	Cyprus, Phoenix
254/BW W9 7/**B008**	p.86, Fig. 99&101	Pick	2.07058	0.83942	18.618	Cyprus, Phoenix
291/BW EII 445/**B078**	p.93&91, Fig. 104	Hoe, large, rounded blade (blank)	2.06993	0.83954	18.592	Cyprus, Phoenix
341/BW?/**B001**	p.84, Fig. 99&101	Pick	2.06598	0.83479	18.774	Cyprus, Phoenix
B272	not published	Rod or nail	2.06619	0.83525	18.768	Cyprus, Phoenix
B280	not published	Handle or a rim	2.07135	0.83809	18.667	Cyprus, Phoenix
GEL 3	not published	Metal frag., lump	2.07094	0.83961	18.585	Cyprus, Phoenix
278/BW EII 17	not published	Chisel, small	2.07462	0.84101	18.624	Cyprus, Phorades
256/BW S 125/?	not published	Pick?	2.07333	0.84092	18.584	Cyprus, Skouriotissa
280/BW G54 236/**B21**	p.86, Fig. 100	Bar fragment (similar found on Cyprus)	2.07178	0.83862	18.708	Cyprus, Skouriotissa
B278	not published	Rod, long	2.07206	0.83675	18.770	Cyprus, Skouriotissa
B279	not published	Rod, bent	2.07226	0.83667	18.771	Cyprus, Skouriotissa
GEL 24	not published	Metal frag., lump	2.07218	0.84098	18.562	Cyprus, Skouriotissa
223/BW P11 14/?	not published	Adze, blade	2.06208	0.83355	18.808	Lavrion
228/BW G18 300/**B095**	p. 93, Fig.107&108	Socketed tool	2.06052	0.83056	18.889	Lavrion
244/BW P53/47	not published	Casting sprue	2.06145	0.83278	18.823	Lavrion
245/BW EI 404		Casting sprue	2.07062	0.83506	18.824	Lavrion
266/BW S 22/**B111**	p.97&98, Fig.109&110	Adze blade frgment with triangular sign	2.06144	0.83248	18.836	Lavrion
267/BW P 37/**B112**	p.97, Fig. 109	Axe blade	2.06145	0.83006	18.895	Lavrion
B284	not published	Axe	2.06700	0.83273	18.807	Lavrion
B295	not published	Nail?	2.06059	0.83224	18.802	Lavrion
SI 11	p.82, Fig. 96	Slab ingot, L. 0.218, W.0.065, Th. 0.01. 0.7kg	2.06272	0.83206	18.849	Lavrion

Table 3: Lead isotope ratios of copper-based artefacts from Cape Gelidonya shipwreck.

SI 13	p.82, Fig. 96	Slab ingot, L. 0.15, W.0.055, Th. 0.012. 0.35kg	2.05916	0.82977	18.908	Lavrion
SI 16	p.82, Fig. 96	Slab ingot, L. 0.209, W.0.08, Th. 0.01. 0.9kg	2.06323	0.83236	18.845	Lavrion
SI 8	p.82, Fig. 96	Slab ingot, L. 0.297, W.0.075, Th. 0.01. 0.9kg	2.06077	0.83066	18.888	Lavrion
SI 9	p.82, Fig. 96	Slab ingot, L. 0.247, W.0.08, Th. 0.008. 1kg	2.05983	0.83024	18.889	Lavrion
218/BW W98/**B224**	p.113, Fig. 126&127	Metal strip/bar	2.06653	0.83303	18.842	Lavrion, Kamareza
B283	not published	tool fragment	2.06802	0.83526	18.760	Lavrion, Kamareza
GEL 4/89	not published	Metal fragment	2.05896	0.83174	18.789	Lavrion, Kamareza
304/BW G119 320/**B127**	p.99&98, Fig.110&109	Adze blade and socket fragment.	2.08706	0.84879	18.477	mixture (Cyp-Sard or Cyp-Wadi Arabah)
297/BW G62 245/**B057**	p.89, Fig.102	Hoe blade, chipped	2.09838	0.85476	18.387	Sardinia
288/BW M4 3/**B062**	p.90, Fig. 103&105	Hoe, Type 3	2.09448	0.85582	18.297	Sardinia, Mt. Nieddu
233/BW G9 66/**B110**	p.97, p.98, Fig.109&110	Adze, unfinished cast?	2.08913	0.84989	18.446	Sardinia, Ozieri
214/BW P52 49/**B223**	p.113, Fig. 126&127	Bar, retangular section	2.09365	0.85453	18.308	Sardinia, Salondra or Funtana Raminoza
337/BW G 413/**B056**	p.88, Fig. 102	Hoe blade, Type 2	2.07956	0.84307	18.628	Taurus, Aladag
296/BW (?)/**B049**	p. 88, Fig. 102&105	Hoe, Type 1	2.07040	0.83533	18.796	Taurus, Aladag-Akdagmadeni
213/BW W9 1/**B221**	p.113, Fig. 126&127	Hoe, flat blank	2.05641	0.82728	18.988	Taurus, Bolkardag
299/BW ?/**B102**	p.95&96&94, Fig.107&108	Axe, half (similar from. Enkomi)	2.05678	0.82934	18.902	Taurus, Bolkardag
308/BW GVII 94 (?)/**B045**	p. 86, Fig. 100&101	Socket, hammered flat	2.05681	0.82797	18.955	Taurus, Bolkardag
B281	not published	Tool fragment	2.05744	0.82926	18.921	Taurus, Bolkardag
292b/BWPII 131/**B055**	p.88, Fig. 102&105	Hoe, flat blank, type 2, the cube stuck on top	2.06009	0.82825	18.962	Taurus, Dundarli-Nigde
301/BW P 58 72/**B101**	p.95, Fig. 107&108	Axe, double, Mycenean type	2.05755	0.82806	18.976	Taurus, Dundarli-Nigde
B264	not published	Sword	2.06988	0.83528	18.788	Taurus, Esendermintepe
262a/BW ?/**B177**	p.107, Fig. 116&117	Handle fragment or part of a tripod	2.10523	0.86254	18.147	Wadi Arabah
B265	not published	Hoe, large	2.11446	0.86934	17.966	Wadi Arabah
B267	not published	Knife, fragment	2.11376	0.86362	18.131	Wadi Arabah
B268	not published	Knife?	2.11507	0.86395	18.141	Wadi Arabah
B285	not published	Hoe, broken	2.10802	0.86448	18.117	Wadi Arabah

Chapter 17

What a long, strange trip it's been: lead isotopes and archaeology

A.M. Pollard[1]

Abstract

This paper casts a backward glance at the long and rather sorry history of the use of lead isotope analysis in archaeology, particularly as a tool for studying the trade in metal around the Bronze Age Aegean. It points out a contradiction in the current situation – that, with recent developments in high resolution ICP technology, we are now in a better position to analyse a large number of samples for lead isotopes, with equivalent precision, and certainly with greater throughput, than we were at the height of the debate, and yet few groups are doing it. This is partly because relatively little of the isotope database was ever fully published, and partly because few people seem prepared to wade in to such muddy waters. It also asks if we were ever really asking the right questions.

Introduction

During the 1980s and 1990s, the Isotrace Laboratory in Oxford became one of a small handful of laboratories in the world dedicated to the isotopic analysis of lead for the purposes of identifying the source of the ancient trade in lead, silver and copper. Led by Noel Gale, it was initially part of Earth Sciences, then Physics, and finally the Research Laboratory for Archaeology and the History of Art, under the overall direction of Mike Tite. For almost two decades, these three or four international groups focussed on critical issues in Mediterranean archaeology, and generated adulation and scepticism in equal measure. A gradual journey away from certainty is discernable, however, even in the titles of the publications over the years. Compare, for example, the positivistic '*The provenance of lead used at Ayia-Irini, Keos*' (Gale et al. 1983) with the more cautious '*Lead isotope characteristics of the Cyprus copper ore deposits applied to provenance studies of copper oxhide ingots*' (Stos-Gale et al. 1997). More clearly revisionist, in a UK context, is the move towards 'EWLIO' and 'IMP-LI's' proposed by Rohl and Needham (1998: see below).

The vast majority of the effort in archaeological lead isotope analysis has been devoted to studying the trade in metals in the Mediterranean Bronze Age. This has been extensively reviewed and summarised (Gale 1991; Gale and Stos-Gale 1992a; Knapp and Cherry 1994; Pollard and Heron 1996: 329). Some of the basic data remains unpublished, and it is sometimes difficult to evaluate the competing interpretations. By the mid-90's, the whole intellectual enterprise had become mired in controversy and unedifying exchange, much of it in the pages of the journal *Archaeometry*, edited by Mike Tite (see, for example, Budd et al. 1993, 1995a, 1995b; Gale and Stos-Gale 1992b, 1993, 1995; Leese 1992; Muhly 1995; Pernicka 1992, 1993, 1995; Reedy and Reedy 1992; Sayre et al. 1992). Since the last round of exchanges in the mid-90's, very little in the way of new archaeological interpretation (at least for the Aegean) has been published. Recent lead isotope studies of metals have tended to focus elsewhere, including South Asian metal icons (Srinivasan 1999), Islamic copper objects (Al-Saad 2000), bronze Punic coins from Sardinia (Attanasio et al. 2001) and Roman silver coins (Ponting

et al. 2003). The latter uses high-resolution Inductively Coupled Plasma Mass Spectrometry with sampling by laser ablation, and is a clear example of the way forward using the new technology available in this area.

And yet the principle that the isotopic ratio of lead measured in archaeological metals (initially lead itself, but more usefully silver and copper), and even in glasses and glazes (Wolf et al. 2003), and human tissue (Gulson et al. 1997), can indicate the geological source of the lead has never been disputed. There was speculation that anthropogenic processing of metals might measurably alter the isotopic ratio of the lead (Budd et al. 1995c; McGill et al. 1999), but this was subsequently shown to be unimportant within existing measurement precision. The idea was, however, subsequently applied to the anthropogenic fractionation of zinc in brass (Budd et al. 1999) and tin in bronze (Budd et al. 1995d; Gale 1997; Yi et al. 1999; Clayton et al. 2002). More contentious still was the display and interpretation of data (see references above), with further exchanges about the normality or otherwise of lead isotope data, and the extent to which provenance could and should be assigned from bivariate plots (Baxter and Gale 1998; Scaife et al. 1999). The latter publication clearly shows that lead isotope data can be fully described using Kernel Density Estimation, without resort to 'confidence ellipses' which assume normality.

As this fades into history, we are left with a contradiction and an important question. The contradiction is that, with the rapid development of high-resolution plasma source mass spectrometers in the last ten years (e.g., Ponting et al. 2003; Niederschlag et al. 2003), the measurement of lead isotope ratios has, relatively speaking, never been easier and more widely available. The question is, then, why is it not being done? Everyone agrees that, scientifically speaking, the method works. The interest in the original questions, such as the source of metals in the ancient Aegean, has hardly lessened (e.g., Knapp and Cherry 1994). And yet, as a method, lead isotope analysis is hardly ever mentioned in polite company. Some of this may well be a legacy of the bitter public debate. There is, however, a much more fundamental problem, which goes to the heart of the long-running debate about the role of scientific method in archaeology (e.g., Pollard 2004) – how can the social and economic questions posed by archaeology be translated into a geochemical research programme? And, of course, how can the results of a geochemical research programme be incorporated into a socio-economic model of past human behaviour?

Lead isotope provenancing

The use of 'chemical fingerprinting' to trace metal objects back to their ore source has been one of the main goals of archaeological inorganic chemistry since the 1930s. Achieving this by chemical analysis is difficult. The relationship between the trace element composition of a metalliferous ore and that of a metal object derived from it is complicated by factors such as variations due to process and temperature, mixing of ores from different sources, deliberate or accidental addition of metals to modify properties of the finished product, and the likely recycling of scrap metal (Wilson and Pollard 2001).

Lead has four stable isotopes, but has a large range of natural isotopic composition because three of them lie at the end of radioactive decay chains (^{206}Pb from ^{238}U, ^{207}Pb from ^{235}U and ^{208}Pb from ^{232}Th), the decay of which supplements the original (primeval) ratios. The fourth, ^{204}Pb, is unchanged from its primeval abundance. The lead isotopic ratio in a metalliferous deposit depends on the geological age of the ore body and the relative proportions of primeval lead, uranium and thorium in the original ore-forming fluids (Pollard and Heron 1996: 312). If present, uranium or thorium in the ore itself will continuously alter the isotopic composition. The discovery in the late 1960s that the lead isotope ratios in an archaeological metal object gives an indication of the ore source (Brill and Wampler 1967), and are apparently unaffected by anthropogenic processing, was a major breakthrough. This was reinforced when it was realized that it applied not only to lead artefacts (relatively rare in the archaeological record), but also to the traces of lead left in silver extracted from argentiferous lead ores by cupellation (Barnes et al. 1974), and to the lead impurities left in copper objects smelted from impure copper ores (Gale and Stos-Gale 1982).

Brill and Wampler (1967) showed that, even with the analytical resolution of the time, it was possible to differentiate between lead from Laurion in Greece, England and Spain, although they noted that an ore sample from north-eastern Turkey fell into the same 'isotope space' as that occupied by three ores from England, thus presaging some of the subsequent interpretational difficulties. The 'downside', if there was one, was that the measurement technique (Thermal Ionisation Mass Spectrometry, or TIMS) was difficult, laborious, slow and therefore expensive. Few isotope laboratories had the necessary combination of technical expertise and interest in archaeology. In time, a 'priesthood' emerged, albeit unconsciously, which effectively controlled the application of the technique to archaeology – the questions which were to be tackled (which is perhaps inevitable), but, more

importantly, the interpretations which could be made from the data – to a degree which encouraged neither criticism or dissent. This is perhaps the first and most important lesson to be learnt from this journey. It is not healthy to concentrate control over the production of scientific data into a small number of hands. It is essential that there exists a critical mass of independent researchers, and also free access to the relevant samples and data, to allow for checking, debate and (if necessary) dispute. This is, after all, the process by which science advances.

Can humans cause fractionation of heavy metal isotopes?

It took nearly 25 years from the first archaeological application of lead isotope analysis before one of the fundamental assumptions was seriously tested from a theoretical perspective (Budd et al. 1995c). This is perhaps another reflection of the negative effect of sub-critical mass in specialised research areas. This assumption was that anthropogenic processing such as roasting the ore, smelting the metal, or secondary extraction processes such as cupellation, produce no measurable isotopic alteration (fractionation), and therefore that isotope measurements from ore and artefact can be compared directly. This was seen as the major advantage of isotopic over trace element provenance studies, since it was known that trace element composition is subject to alteration by a range of factors.

Not that the issue of fractionation had been ignored by the pioneers of the method. Barnes et al. (1978) compared the lead isotope ratios of galena (PbS, lead sulfide – the principal lead ore mineral) with that of the lead smelted from it, with litharge (PbO) prepared from the smelted lead, and of a K_2O-PbO-SiO_2 glass and a pigment ($Pb_2Sb_2O_7$) prepared from the same lead. They reported no difference in any of the measured ratios, within the measurement precision then available. Hindsight now suggests that these experiments may not have been those expected to give the most significant fractionation, and that this is not necessarily proof of the lack of fractionation in all processes.

If a liquid is made up of molecules which are chemically identical but having different molecular weights because of isotopic effects (such as $H_2{}^{16}O$ and $H_2{}^{18}O$), then kinetic theory predicts that the lightest isotope will preferentially enter the vapour phase on evaporation, leaving the liquid enriched in the heavier isotope and the vapour phase in the lighter. If evaporation goes to completion or the system is left to equilibrate, then there is no difference between the isotopic ratio of the liquid and the vapour. However, if the vapour phase is continuously removed, then the lighter isotope will be preferentially removed and the liquid will become gradually enriched in the heavier isotope. This is termed non-equilibrium evaporation, the mathematics of which were published by Mulliken and Harkins (1922). Scaife (1993) was the first to demonstrate that non-equilibrium evaporation from a liquid could have a significant effect on the isotopic ratio of lead, providing the non-equilibrium losses are sufficiently large. Taking the published lead isotope field for Laurion it was shown that 40% non-equilibrium losses would be sufficient to move a sample from the centre to the edge of the field, and above 60% would remove it completely from the field (Pollard and Heron 1996: 235). In the experiments reported by Barnes et al. (1978) the yields were much higher than this (i.e., the losses were much lower) for each stage – 98.6% yield for lead recovery from galena, and 95% for the production of litharge. Hence it is not surprising that no measurable fractionation was observed in these experiments.

Do any ancient processes show such high losses, and can they be regarded as non-equilibrium? The most likely process in the lead-silver system is cupellation, in which a liquid of around 99% lead and 1% silver is converted by preferential oxidation to an alloy with more than 95% silver – a lead loss in excess of 99%. Experiments by Pernicka and Bachmann (1983) on the cupellation of silver from Laurion galenas had concluded that the process did not fractionate. In the 1990s a series of simulated laboratory metallurgical processes were carried out on galenas and lead, and, despite occasionally achieving significant lead losses, isotopic measurements showed no significant change in the ratios (Budd et al. 1995d). This suggests that the non-equilibrium evaporation of lead during most ancient processing techniques is unlikely to have been a significant source of isotopic fractionation. Whether this would still be the case if the measurements were to be repeated using the newest generation of high-resolution inductively-coupled plasma mass spectrometers (with a ten-fold increase in precision over TIMS) is an open question, and one which might profitably be explored. It is not, however, likely to be a confounding factor in isotopic provenancing, but might be a useful process indicator.

This excursion into a consideration of non-equilibrium thermodynamics was not, however, entirely wasted. Subsequent application of the theory of non-equilibrium evaporation to other metallic systems (specifically tin in ancient bronzes) gave rise to speculation that it might be a potentially fruitful

method for quantifying the degree of recycling of copper alloys (Budd et al. 1995d; Yi et al. 1999). Clayton et al. (2002) subsequently published precise determinations of the isotopic composition of metallic tin and cassiterite using high resolution Multi-Collector ICP-MS showing that natural isotopic fractionation of tin can now be measured in this system. This now opens up the prospect of addressing scientifically one of the most intractable questions in archaeology – where did all the tin come from in the European Bronze Age (e.g., Budd et al. 1994)?

Perhaps the most interesting alloy to which to apply the consideration of induced fractionation is brass (copper-zinc), given the volatility of zinc and the uncertainty over historical production methods (Pollard and Heron 1996: 198). Brass melting experiments at 1100°C followed by quadrupole ICP-MS zinc isotope ratio measurements of the resulting alloys suggested that the non-equilibrium evaporation model is appropriate to this system (Budd et al. 1999). These data indicated that the change in isotope ratio of the residual alloy would be measurable by quadrupole ICP-MS for zinc losses by evaporation of more than about 30%. It is unlikely, however, that measurements at the precision available from Q-ICP-MS would be sufficient to distinguish between the two principal historical brass-making processes (the older cementation process, and the more recent direct process), although again more precise measurements using a multi-collector ICP-MS may well be. This suggests that this may also be a profitable area to return to with newer instrumentation.

To complete the picture of the evolution of ideas about heavy isotope studies in archaeology, Gale et al. (1999) reported the measurement of natural variations in the isotopic composition of copper in both natural copper minerals and in some ancient metal artefacts. Significant isotopic variations were found in both, suggesting that there may be potential for copper isotope analyses in metal provenance studies, at least as a supplement to lead isotope studies. This study also suggested that measurable isotopic fractionation of copper does not occur during ancient smelting and refining processes.

When is an orefield not an orefield?

The second and perhaps most vitriolic area of debate centred on the presentation and interpretation of lead isotope data. This involves consideration of the statistical, archaeological and geological definition of the extent of a 'lead isotope field', and the subsequent interpretation of lead isotope data from archaeological material. In presentational terms, all agree that the measured data can be completely presented using a pair of bivariate diagrams – one plotting $^{208}Pb/^{206}Pb$ against $^{207}Pb/^{206}Pb$, and another, less often used, showing $^{204}Pb/^{206}Pb$ against $^{207}Pb/^{206}Pb$. Key questions include how can the isotopic extent of orefields on such diagrams be predicted from a relatively small number of samples, what shape should they be, do they form discrete or overlapping groups, and how can 'unknowns' (isotopic measurements from archaeological samples) be assigned to the appropriate source group?

A good knowledge of the ore geology of the area is clearly necessary before isotopic (or any other) provenancing work is undertaken. Fieldwork is essential to collect suitable samples, since ancient mining is often in areas which are now not considered to be economically viable, and the data therefore are often not available in the geological literature. It is theoretically important only to compare metal artefacts with the kind of ore from which they may have come, such as silver objects with argentiferous galenas, or copper alloys with copper minerals. Thus isotopic ore fields should be constructed only from relevant minerals, rather than assembled from a range of minerals and metallurgical debris. Of necessity, this principle is sometimes sacrificed in order to get enough data to define a 'field'. A second principle is that only samples of the ores available to ancient miners should be used. Clearly data from deposits so deep that no ancient process could possibly have exploited them, or from ores which are so finely dispersed that only modern extractive metallurgy can win metal, are not useful for archaeological purposes. A research strategy must attempt to balance up the advantages of having a larger number of samples against these constraints.

In the early days of lead isotope analysis simple bivariate plots of (usually) $^{208}Pb/^{206}Pb$ against $^{207}Pb/^{206}Pb$ were used to display the data, and the extent of the isotope fields shown by envelopes of various shapes hand-drawn around the data from each ore source (see, for example, Pollard and Heron 1996: 332). If the isotopic ratios are assumed to be normally distributed, then isotopic field boundaries can be calculated and plotted as 95% 'confidence limits' around groups of points. If this is not sufficient to separate out the various sources, linear discriminant function analysis (DFA) has sometimes been used to distinguish between pre-defined groups. All of these approaches are open to criticism. The multivariate normality of lead isotope data has now been shown to be questionable and an unsafe assumption (Baxter and Gale 1998). The models used by geologists to

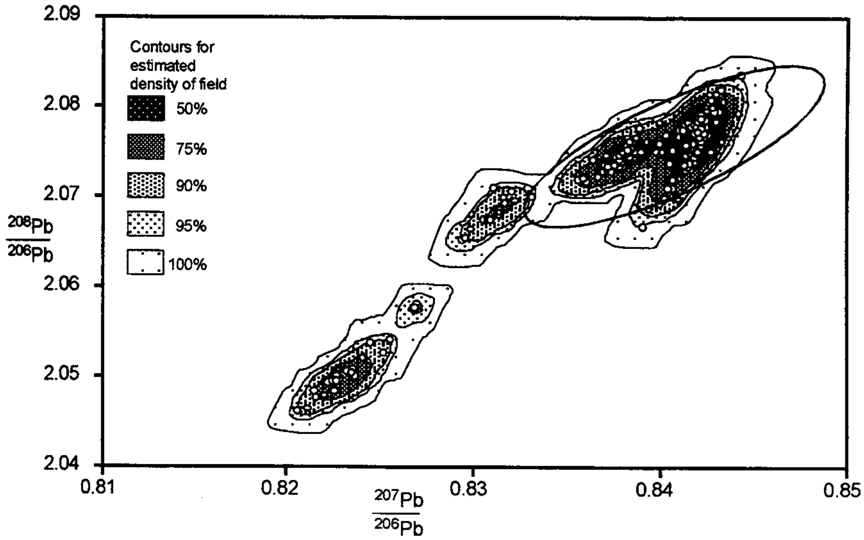

Figure 1: Kernel Density Estimate of part of the Troodos orefield, Cyprus (data from Gale et al. *1997). The ellipse shown is the one used to represent the Cyprus field in many previous publications. Figure from Scaife* et al. *(1999).*

describe the evolution of lead isotope compositions in ore deposits (see Pollard and Heron 1996: 312) show that they develop along tightly constrained lines in isotope space. In some dimensions, therefore, there will be more sharply defined limits than others – not a uniform 'fall-off' in all directions, as would be the case with normally distributed data. If we need to predict the size of parent fields from a small number of samples, then account must be taken of these geological models, rather than attempting to calculate them from assumptions about underlying distributions (Scaife et al. 1996). Following this, the practice assigning an unknown sample to a parent ore group on the basis of the shortest relative distance to each of the ore group centroids (as is done in DFA) is not a good way of assigning group membership.

Because of improvements in desk-top computing power over the last ten years, lead isotope data can now be fully visualised in a rotatable three-dimensional plot defined by the three independent isotopic ratios. If all the available data points from an ore body are plotted (with their error bars) onto such a diagram, then this gives the most valid description of that ore body's isotope field that is possible without geochemical modelling (Scaife et al. 1996). If an unknown sample falls within the limits of this isotope field then it cannot, on isotopic evidence alone, be excluded from that field. If, on the other hand, it lies outside these limits, then it cannot be attributed to that field. The problem then reduces to one of defining the limits of the isotope field, taking into account geochemical ore evolution models, together with sampling and measurement uncertainties.

It follows from this that the concept of what constitutes an 'outlier' is important, since it is common practice for 'outliers' to be omitted from the definition of isotopic fields. Scaife et al. (1996) have argued that if an accurate and precise measurement is made on a sample which is geologically securely tied to a specific ore deposit, then it cannot be classified as an outlier, no matter how different it is isotopically from other samples in that deposit. The isotopic homogeneity of lead sulfide deposits is usually less than 1% although some deposits show an order of magnitude greater variation, such as the Pb-Zn sulfides in the Upper Mississippi Valley. Much of this variation can be found within a single crystal in such deposits (Pollard and Heron 1996: 326). It is not inconceivable therefore that large variation might be found within a small number of samples taken from such a deposit, which should not lead to the extreme value being discarded as an 'outlier'. Such an 'outlier' identified on purely isotopic grounds should in fact be taken as a clear indication that the 'isotopic field' has been defined too tightly. This dictum might be too idealistic in some cases (e.g., if the sample is very low in lead, in which case the isotope measurement is more difficult) but it must be a starting point for the definition of isotopic fields. In general, all samples collected from a particular deposit must be used in the definition of its isotope field, unless an error has occurred, or the measurement is demonstrably dubious for some reason.

All of this analysis simply supports the opinion of Pernicka et al. (1990) – that the use of conventional bivariate plots is preferable to the application of

multivariate normal statistics or the use of Discriminant Analysis. Simple bivariate plotting does not, however, lead to an estimate of the true extent of the parent isotope field, which is a problem if only relatively few samples are available (as is usually the case). Kernel Density Estimation (KDE: Baxter et al. 1997) offers the prospect of building up an estimate of the true shape and size of an isotope field whilst making few extra assumption about the data. Scaife et al. (1999) showed that bivariate KDE plots could be constructed for the Troodos Mountain orefield, Cyprus using published data from Gale et al. (1997). Firstly the data were rotated onto new axes parallel and orthogonal to the 121 Ma isochron. This represents a reasonable approximation to the main axis of variation of the data. A KDE was then carried out, using kernels parallel to these new axes and a density estimation calculated. The density estimation was then rotated back to the original isotope ratio axes, resulting in Figure 1. Shown for comparison on this figure is the 'Oxford ellipse' derived from the same data. The Kernel Density Estimate appears to be a much better representation of the original data than the imposed ellipse, and suggests that use of this ellipse might underestimate the true extent of the orefield, and hence lead to misclassification of the source of ancient artefacts. This suggests that KDE techniques offer a positive and more reliable way forward for the presentation and interpretation of lead isotope data in the future.

Answers in search of a question, or getting a better question?

It has been stated elsewhere that one of the major goals of chemical analysis of metals, and then lead isotopic analysis, was to 'trace metal objects back to their ore source, and hence reconstruct prehistoric economic contacts' (Pollard and Heron 1996: 302). 'Hence' here is a big word. With hindsight, it can be seen that the two parts of this aim are not always as well articulated as they need to be. Subject to the considerations outlined above, it is not disputed that the first part of this goal can be achieved to some degree. Whether the second part is achievable at all depends on how well expressed the archaeological problem has been in scientific terms, and how well constructed the analytical programme has been to address this question.

As the subject of study of chemical provenance, ancient metals suffer from all of the difficulties listed elsewhere (Wilson and Pollard 2001). The use of lead isotopes circumvents many of these problems – in fact, the only likely drawback is if significant quantities of lead have been introduced from a different source, either by the recycling of scrap or the deliberate addition of lead to control fluidity during casting. Irrespective of these considerations, the lead isotope method of provenancing has some inherent limitations. In their study of the British sources of copper in the Bronze Age, Rohl and Needham (1998) show that, despite the fact that non-ferrous mineralization in the British Isles occurs in four different geological environments, the isotope data shows no systematic differences between them. In fact, the authors present the data from all British and Welsh ore sources as 'EWLIO' – the 'English and Welsh Lead Isotope Outline'. They also show how EWLIO relates to Scottish, Irish, French and German sources – in all cases, the data overlie EWLIO, although they often extend beyond it. Some particular attributions can be made (e.g., certain parts of Cornwall have high uranium, which gives a highly distinctive lead isotope signature), but it seems clear that isotope data in this case is insufficient to uniquely characterize the material. This is an important but disappointing finding, confirming the problem first identified by Brill and Wampler (1967), who observed a single sample of Turkish ore overlapping the field defined by three English ores. Not all geographically discrete ore fields are isotopically distinct, and no amount of statistical manipulation can separate groups which fundamentally overlap in the measured parameters.

As a result of this ambiguity, attempts have been made by Rohl and Needham (1998) (amongst others) to combine isotope data with trace element information, specifically by introducing the concept of IMP-LI's – 'impurity composition and lead isotope composition'. Each IMP-LI is said to represent *'a stock of metal in circulation which might either be similar to the character of a specific source, or alternatively be a complex but relatively coherent amalgam of different metals'* (Rohl and Needham 1998: 84). Since isotopic and chemical characteristics are independent of each other neither data set is given primacy in the analysis, and therefore these IMP-LIs are said to be more robust than either data set on their own. Objects from 12 major typological groupings of British Bronze Age metalwork assemblages are classified into 23 IMP-LIs. The authors state *'Previous classifications, ... have certainly not been invalidated...; on the contrary, the chemical differences observed find much support in lead isotope ratios. However, the latter do show that at times the chemical patterns are not adequate discriminators between different inputs to the metal supply'* (Rohl and Needham 1998: 176). The process occasionally also works in

reverse – groups with similar isotopic ratios have different chemical compositions.

This suggests that (with hindsight) we perhaps have been asking the wrong questions all along. It appears that, despite now having good archaeological evidence for early mining for some parts of the world (including the UK), we still cannot easily determine the actual ore source (i.e., the mining site) for well-established groups of metalwork. Does this matter? Perhaps we should be focussing more on the changes that show up in the chemical and isotopic record in the metals themselves, since these directly reflect changes in some aspect of human behaviour (a view which might be termed 'processual provenance'). This might be the result of changes in patterns of ore exploitation, or technological change in extractive metallurgy, or changes to the pattern of metal circulation and recycling. Whatever the cause, the result is something tangible, and perhaps of more direct archaeological interest, ultimately, than knowing that the metal for a particular object came from a particular mine site. Although moving away from the original concept of provenance, it might be argued that the relatively simple detection of *change* in the material record is valuable information when interpreting that record. This is particularly the case if such a change is contemporaneous with other changes observed in the archaeological record – stylistic influences, mortuary patterns, stratigraphic sequence, or whatever. In such cases, it might be reasonable to observe that some variation has occurred to the metal in circulation as a result of social change, rather than necessarily assuming a simplistic shift in raw material extraction patterns or technological change (e.g., Begemann et al. 1995).

The onward journey

Beyond agreeing the fundamental point that lead isotope ratios in metals (and other materials, including glasses, glazes, bone and teeth) are indicative of the source of the material, virtually everything else has been disputed over the last 20 years. The debate has not always adhered to the highest standards of scientific exchange (allegedly, for example, certain parties were threatened with arrest if they attempted to visit a particular ore deposit!). The time has clearly come to look forward, not least because advances in measurement techniques and the power of data manipulation have increased immeasurably in the last five years, and new insights are undoubtedly possible.

Substantial efforts have been made in recent years, particularly by Mike Tite as editor of the journal *Archaeometry*, to publish the backlog of accumulated lead isotope data, particularly for the ore sources in and around the Aegean (e.g., Rohl 1996; Stos-Gale et al. 1995, 1996, 1998; Gale et al. 1997; Sayre et al. 2001). There is still, however, more to be published before we have a full picture of the work carried out over the last 25 years.

The key question to address now is 'what is the question?' – what kind and level of information is useful in the context of the current social models of trade and exchange for the region being studied? It has been suggested in the past that provenance studies are misdirected – asking the wrong question, or an irrelevant question (thus eliciting the 'so what?' response!). Much effort, particularly in the field of metal studies, has been expended in identifying the *exact* source of the raw materials, even down to particular mines. It might be argued that the archaeological framework within which these studies need to be interpreted is not sufficiently well-developed to accommodate such precise information – precise models of social structure, trade specialization, and modes of exchange are often singularly lacking. Perhaps, as argued above, less is more – less specific scientific information may be of more immediate relevance. Particularly in the case of metals, what is actually of greater archaeological significance, at least in the short term, might be the knowledge that *something* has changed, rather than the specifics of *what* has changed.

Provenance studies of inorganic artefacts are not currently the most 'fashionable' branch of archaeological science, and yet the capacity to carry out large-scale studies of this type is now more widely available than ever before. Advances in analytical instrumentation, and specifically the high throughput capacity, multi-element sensitivity and isotopic resolution of the new generation of High-Resolution Inductively Coupled Plasma Mass Spectrometers means that capacity is no longer limited by analytical restrictions. In particular, with sensitivities for isotopic ratios such as lead comparable to (if not better) than that of conventional TIMS instrumentation (Halliday et al. 1998) the more widespread use of H-R ICP MS machines will herald a new age of relatively rapid and cheap isotopic and chemical studies of archaeological material. This is already happening with lead isotopes (Niederschlag et al. 2003; Ponting et al. 2003), but also with isotopes of copper (Gale et al. 1999), tin (Clayton et al. 2002), and even osmium isotopes in gold (Junk and Pernicka 2003). It is likely that many of the questions raised about the possibility of anthropogenically-induced fractionation could be profitably revisited with these

instruments, with a view to understanding changes in ancient metal processing. We may look forward to a future in which the utility of heavy isotope studies in archaeology is not limited by analytical capability, but more by the quality of the definition of the archaeological problem.

In trying to summarise the journey through the last 20 years of lead isotope applications in archaeology, it is tempting to recall the line by Woody Guthrie 'I ain't ever got nowhere yet, but I got there by hard work'[2]. This is too negative – we have got somewhere, but perhaps we're not entirely sure where it is. It is probably better to remember the immortal line of the Grateful Dead – 'What a long strange trip it's been'[3]. The trip, however, is not yet over. We simply have to be prepared to use the new modes of transport available.

Notes

1 Research Laboratory for Archaeology, Univeristy of Oxford, Dyson-Perrins Building , South Parks Road, Oxford, OX1 3QY.

2 Woody Guthrie, "Talkin' Hard Luck Blues". Re-released on 'The Very Best of Woody Guthrie', Music Club, 1992.

3 Grateful Dead, "Truckin'". American Beauty, Warner Bros., 1970.

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A response to the paper of A.M. Pollard: What a long, strange trip it's been: lead isotopes and archaeology

Noël H. Gale[1]

Editors' note

The lead isotope controversy of the 1990s continues to provoke disagreement. In the accompanying chapter, Mark Pollard, one of the protagonists, gives his personal view of the controversy and its implications. Although Pollard's contribution was refereed, just before publication we received a set of late comments from Noël Gale, who was Director of the Oxford Isotrace Laboratory through most of the 1980s and 1990s and who was at the centre of the debate at that time. Gale points out what he considers to be errors in Pollard's interpretation. For the purpose of balance, we include a short commentary by Gale, focusing upon what he considers the most contentious points. Elsewhere, Zofie Stos presents an example of the on-going application of lead isotope analysis to produce useful archaeological information.

Introduction

At the height of the controversy over the application of lead isotopes to the provenancing of Bronze Age metalwork, Mike Tite produced an outstanding paper "In Defence of Lead Isotope Analysis", for the journal *Antiquity* (1996). The paper by Pollard seems to me to contradict or ignore a number of the important points made by Tite in that paper, and I am grateful to the editors for allowing me to set the record straight. It seems apposite to begin by quoting Tite (1996: 959) directly:

> "The recent *Antiquity* paper by Budd et al. (1996), 'Rethinking the quest for provenance', is the latest in a series of polemical papers on archaeometallurgy by the Ancient Metallurgy Research Group at Bradford. Having started with the appearance of arsenical copper in Britain in the Early Bronze Age (Budd et al. 1992), this series has now moved on to the application of lead isotope analysis to copper provenance studies. These papers contain very little, if any, new scientific data but instead attack established procedures and interpretations."

Tite (1996: 961) comments further that:

> "Although papers criticizing earlier work can play an important role in advancing a subject, it is crucial that such papers provide a balanced overview of the current state of research. An excess of partisan papers, attacking what are essentially 'straw men', risks bringing lead isotope analyses, and indeed archaeological science itself, into disrepute and is thus a disservice to the subject."

I would contend that Pollard's present paper falls into the class of papers criticized by Tite, and contains some direct errors, of which the first concerns the statistical treatment of lead isotope data.

The Kernel Density Estimate representation of the Cypriot ore deposits

Pollard writes:

> "The density estimation was then rotated back to the original isotope ratio axes, resulting in Figure 1. Shown for comparison on this figure is the 'Oxford ellipse'

derived from the same data. The Kernel Density Estimate appears to be a much better representation of the original data than the imposed ellipse, and suggests that use of this ellipse might underestimate the true extent of the orefield, and hence lead to misclassification of the source of ancient artefacts."

But the KDE representation computed by Scaife (Scaife et al. 1999, Fig. 6) is based on all the Cypriot ore deposit data (nearly 200 data) which Oxford published in 1997, whilst Pollard's superimposed 'Oxford ellipse' is based on only the roughly 43 data published up to 1997. This is a strictly incorrect and false comparison. If an ellipse is correctly constructed using all the 1997 data, as shown in Fig. 1 of the present paper, it encloses the whole of the KDE representation, the alleged discrepancy disappears, and Pollard's argument collapses.

It should also be pointed out that Stos-Gale et al. (1997: 118) explained in 1997 and later papers (Gale 1999: 111–112, 119–120) that we no longer used ellipses, or statistics, and had reverted to the simple two bivariate plots and point-by-point comparisons of LIA for artefacts and ores [as is also the practise of Begemann, Hauptmann, Pernicka and other authors such as Pinarelli (2004) andValera et al. (2002)].

Pollard's present paper repeats criticism made in the past by the Bradford Group about the use of multivariate statistics to interpret lead isotope data. This directly illustrates the strange trip introduced into lead isotope studies by the interventions of the Bradford Group, for it was Pollard himself who first introduced multivariate statistical interpretation into lead isotope work (see Gale 1989: 489, Fig. 13).

Possible fractionation of lead isotopes during ancient metallurgical processes

Lead isotope provenancing would fall at the first hurdle should fractionation of lead isotopes occur during ancient metallurgical processes. Pollard feels that the evidence against the occurrence of such fractionation adduced by Barnes et al. (1978) is insufficient and, in a circuitous discussion, suggests that Budd et al. (1995) and Pernicka and Bachmann (1983) had shown that such anthro--pogenic fractionation does not occur. The problem is, as Tite (1996) wrote, that these authors published no numerical data to back up their assertions, in practise leaving the subject in limbo. However Tite (1996: 960) wrote that numerical data published by Gale and Stos-Gale (1996a) "…demonstrated that lead isotope fractionation did not occur for silver subjected to roasting, smelting, cupellation and refining".

Homogeneity of isotope deposits

Pollard writes:

"The isotopic homogeneity of lead sulfide deposits is usually less than 1% although some deposits show an order of magnitude greater variation, such as the Pb-Zn sulfides in the Upper Mississippi Valley. Much of this variation can be found within a single crystal in such deposits (Pollard and Heron 1996: 326). It is not inconceivable therefore that large variation might be found within a small number of samples taken from such a deposit, which should not lead to the extreme value being discarded as an 'outlier'".

I do agree that confirmed 'outliers' should not be discarded. But the Upper Mississippi Valley (UMV) is not a single ore deposit, but a huge ore district of over 10,000 square kilometres, containing many individual ore deposits which individually mostly have uniform lead isotope compositions – this is reviewed in Gale (1989: 472–473) and in Gale and Stos-Gale (2000: 512–513 and 542–543). Moreover Farquhar and Fletcher (1980, 1984) have successfully provenanced artefacts to UMV ore deposits. To use the UMV as a model for Mediterranean ore bodies is a false comparison.

Ongoing lead isotope work

Pollard writes:

"Since the last round of exchanges in the mid-90's, very little in the way of new archaeological interpretation (at least for the Aegean) has been published."

The attached reference list includes over 55 papers (chiefly for the Aegean) published since 1995; this list is certainly not complete. None of this had anything to do with the controversies, after which new LIA interpretations continue to be published. Pollard is clearly misinformed here.

Do we know where we are?

Pollard writes:

"In trying to summarise the journey through the last 20 years of lead isotope applications in archaeology, it is tempting to recall the line by Woody Guthrie 'I ain't ever got nowhere yet, but I got there by hard work'. This is too negative – we have got somewhere, but perhaps we're not entirely sure where it is. It is probably better to remember the immortal line of the Grateful Dead – 'What a long strange trip it's been'. The trip, however, is not yet over. We simply have to be prepared to use the new modes of transport available."

I believe that we have got somewhere and know where it is, as shown by the attached publication list.

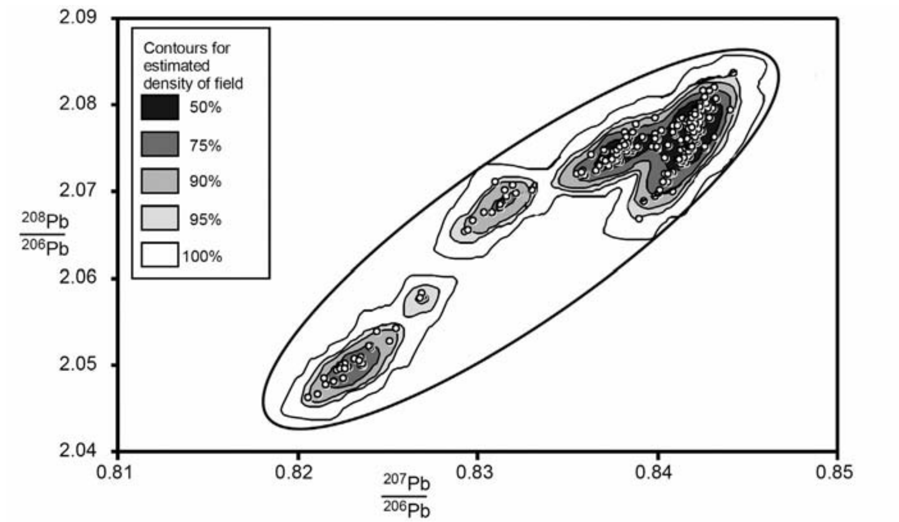

Figure 1: Kernel Density estimate of the Troodos ore deposits on Cyprus (data from Gale et al. 1997). The elipse shown embraces all of the 1997 data, but should not be used to define an overall "Cypriot field", because the ellipse clearly encloses isotopic space not occupied by any isotopic data for the Cypriot ores. Figure based on Scaife et al (1999).

A particular case in the Mediterranean is that of the copper oxhide ingots, the provenance of which had been identified by Muhly (1977) as a major research priority, fundamental to understanding the Bronze Age metals trade. This was necessarily a long journey in that archaeological permission to sample the ingots involved many countries – Cyprus, Greece, Italy, Turkey, Bulgaria, Syria, Israel, USA, UK etc. Furthermore the ore sources to be sampled were widespread around the Mediterranean. Lead isotope analyses revealed something that no one had previously guessed: that the majority of oxhide ingots were not made from copper from a range of Cypriot ores, but only from copper from the Apliki ore deposit, and that the oxhide ingots on Sardinia came from this same Apliki source, but the nuragic artefacts were made from Sardinian copper ores (Gale 1999, 2006; Stos-Gale and Gale 1992; Begemann et al. 2001).

In a rather rare occurrence in archaeometry we even have independent confirmation of the situation in Sardinia from the work of Begemann et al. (2001), and Pernicka (2005, pers. com.) has confirmed our lead isotope analyses of 147 Uluburun oxhide ingots and 23 ores from Apliki. These considerable successes of lead isotope analyses in the Mediterranean have yet to be assessed fully from the archaeological point of view, but this is not because there is some insuperable problem in archaeological theory. It is also clearly the case that there is still more to be discovered even about oxhide ingots, particularly the LMIB ingots from Hagia Triadha and Zakros (Gale and Stos-Gale 1986), and ingots from Uluburun (Gale and Stos-Gale 2005). But that is normal in archaeology and science. Finally, the papers by Tite (1996) and Gale and Stos-Gale (2000) may possibly provide more balanced guides to the application of lead isotopes in archaeology than does the present paper by Pollard.

Note

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Chapter 18

The juice of the pomegranate: processing and quality control of *alumen* in antiquity, and making sense of Pliny's *phorimon* and *paraphoron*

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Abstract

Recent geoarchaeological work on Melos has assisted in the technical characterisation of Melian *alumen* (alum – aluminium sulphate) which was praised by Pliny (1st c. AD) as the best. This paper considers the means by which Melian *alumen* would have been processed and investigates Pliny's suggestion that the juice of the pomegranate was used as a test for its purity. Regarding its processing, it demonstrates that *alumen* could have been purified by removing impurities by partial crystallisation of solutions evaporated using geothermal energy (solfatara) as a heat source. Our experiments also offer an explanation as to the nature of the 'liquid' and the 'solid' *alumen* referred to by Pliny (*Nat. Hist.* 35, 184 and 185) as *phorimon* and *paraphoron* respectively, and an issue of much scholarly debate. Regarding its quality control, it is demonstrated that the pomegranate juice would have been a sensitive test for presence of iron impurities in *alumen*, with ~300 ppm needed to turn the solution a dark purple.

Introduction

The exploitation in the Classical/Roman period in the Aegean of industrial minerals, including the 'earths' from various localities as well as sulphur, miltos and *alumen*, is known from Theophrastus, Pliny, Dioscorides and others who highlight their varied applications and their importance as pigments, medicines or mordants. Alum (Latin – *alumen*; Greek – *stypteria*) is a general term encompassing a variety of aluminium sulphates. *Stypteria* first appears as a tradable commodity in linear B tablets (tu-ru-pte-ri-ya) from Pylos dating to the Late Bronze Age (Bennett and Olivier 1973) as well as Tiryns and Knossos in association with other commodities. The sources and material traded as *stypteria* in the Bronze Age may or may not have been the same as for *alumen* in the Classical/Roman period. Pliny in the 1st c. AD certainly stresses its use both as a medicine (*Nat. Hist.* 35, 185–190) as well as a mordant (*Nat. Hist.* 35, 183). There is no archaeological evidence for the extraction of *alumen* in Melos in the Bronze Age but given that even the mining activities of the Roman period are difficult to locate in view of modern large scale extraction, earlier evidence might be indirect and certainly less obvious (Photos-Jones and Hall, in preparation).

The modern word 'alum' is clearly derived from *alumen* (Singer 1948) and was presumably adopted, before its chemical identity was established, for substances which had the same properties and uses. Alum's economic importance in antiquity and the medieval period throughout the Mediterranean and northern Europe is well known (Singer 1948; Millard 1999; Cardon 2003). Alum was used in the dyeing industry, not only as a mordant for fixing, or making 'fast', the dye on the wool or linen fibre but also as a means of enhancing or brightening the colour of the yarn (Singer 1948; Cardon 2003). The chemical composition of alum was pursued through the 18th century; the metal base was isolated and named aluminium and alum was eventually recognised by Dalton in 1810 to contain mainly K^+, Al^{3+} and SO_4^{2-} (Singer 1948). While 'alum' has long been considered synonymous with 'potassium alum', the current mineral name approved by the International Mineralogical Association (http://www.mindat.org/min3267.

Table 1: Minerals mentioned in the paper.

Name	formula	Notes
alum	$(Na,K,NH_4)(Al,Fe^{3+})(SO_4)_2.12H_2O$	A group name for aluminium sulphate minerals that can contain diverse cations.
alunite	$(K,Na)Al_3(SO_4)_2(OH)_6$	A potential source of alum, by slaking.
alunogen	$Al_2(SO_4)_3.17H_2O$ (sometimes $.16H_2O$)	An alum-group mineral.
arcanite	K_2SO_4	
epsomite	$MgSO_4.7H_2O$	Epsom salts.
gypsum	$CaSO_4.2H_2O$	
halite	NaCl	Common salt.
jarosite	$KFe_3(SO_4)_2(OH)_6$	Contains ferric iron, Fe^{3+} (oxidised iron).
K-alum *or* potassium alum *or* potash alum *or* kalinite	$KAl(SO_4)_2.12H_2O$ (sometimes $.11 H_2O$)	The main alum-group mineral.
melanterite	$FeSO_4.7H_2O$	Contains ferrous iron, Fe^{2+} (reduced iron).
thenardite	Na_2SO_4	

html) but often abbreviated to K-alum (see Table 1), the present-day correct and appropriate use of 'alum' is as a mineral *group name* for various aluminium-rich and similar sulphate minerals which include K-alum and alunogen (Table 1). 'Potash alum' is the term often used commercially for K-alum. There are many related/similar aluminium sulphate salts with variable contents of cations, anions and molecular water making identification of suspected alum group minerals and salts reprecipitated from solution difficult (see Nordstrom 1982). Because it is aluminium that plays the active role in the main uses of alum salts (Singer 1948), and we are investigating their production in antiquity, we retain here the Latin term *alumen* and will assume that it refers to soluble aluminium sulphate minerals with or without additional cations.

Our research into Melian *alumen* has identified various types of deposits on Melos and has confirmed that it is geothermal activity which underlies the geological processes leading to their formation. Melian *alumen* includes both alunogen and K-alum usually occurring in efflorescences in association with other sulphate minerals. It is also clear that these deposits of *alumen* would have been available for exploitation in Roman times (Photos-Jones et al. 1999; Hall et al. 2003a,b). There is no evidence, such as roasting kilns, for the exploitation of alunite which is present in SE Melos in association with kaolinite and quartz as a product of decomposition of the local volcanic rocks.

Pliny (*Nat. Hist.* 35, 184) identified ten sources for *alumen*, but thought that Egypt and Melos provided the best:

> *laudatissimum in Aegypto, proximum in Melo. huius quoque duae species, liquidum spissumque. liquidi probatio ut sit limpidum lacteumque, sine offensis fricandi, cum quodam igniculo caloris. hoc phorimon vocant.* (*Nat. Hist.* 35, 184)

> The most famous is that of Egypt, then comes that of Melos. The Melian, like the Egyptian, is divided into two kinds. The liquid one is clean and milky and does not irritate the fingers when rubbed and should be flame-coloured. It is called *phorimon*. (Translated by the authors from the Greek of Levidis 1994, including notes.)

The question of what precisely was meant by 'liquid' *vs* 'solid' *alumen* has been a subject of debate by various scholars (Singer 1948; Healy 1999) and this paper certainly does not intend to throw additional light on the ongoing and often difficult-to-follow discussion of the many 'species and genera' of alumen reported by Pliny. One way to differentiate between the two states may lie in the use of potentially different reagents for the identification of impurities in each:

> *an sit adulteratum, deprehenditur suco Punici mali; sincerum enim mixtura* ....(**text missing in original**).... *alterum genus est pallidi et scabri et quod inficatur et galla, ideoque hoc vocant paraphoron.* (*Nat. Hist.* 35, 184–185)

> If it is contaminated, this fact becomes immediately obvious with the use of pomegranate (Punici mali = apple of Phoenicia) juice. The unadulterated *alumen*, when mixed.............the other species (ie the solid one) is light coloured (palid) and granular and this species can be coloured (dyed) with the juice of the oak (galla) and that is why they call it *paraphoron*. (Levidis *op cit*)

From the above it can be deduced that pomegranate juice is used in testing impurities in *phorimon* (the 'liquid' form of *alumen*) and oak gall juice is used for the *paraphoron* (the 'solid' form). Because of the modern understanding of the use of iron sulphate and oak gall juice to produce iron tannates in early inks, it seems clear that both pomegranate and oak gall juice were used to detect iron impurity in *alumen*. (Singer 1948; Healy 1999). But was iron the sole impurity being detected or could there have been another impurity such as manganese? In other words do we have two tests (pomegranate and oak gall juices) for the same impurity (iron) in different substances (*phorimon* and *paraphoron*) or could there have been two different impurities (say iron and manganese)? And what are the active ingredients in the two types of juice?

The aim of this investigation is to present the results of field-based and laboratory-based experiments that consider *alumen* processing on Melos and possible purification thereof in an attempt: a) to establish whether there are indeed two physical states of *alumen* (corresponding to 'liquid' and 'solid'); and b) to ascertain whether pomegranate juice is a sensitive enough test for minor impurities. Crucial to the investigation is Pliny's implication that visual inspection, i.e. the colour white, was not a satisfactory means of appraising purity in *alumen* and that a manufacturer/merchant's concern would have been to insure just that.

Processing of alumen: field experiments

Field experiments were aimed at establishing the manner by which processing /purification of *alumen* could have taken place in antiquity. The experiments took into consideration the account by Millard (1999) of industrial production of alum from the roasting of pyritic aluminous shales in the 17–18th centuries AD in Britain. Roasting for the purpose of producing aluminium sulphate was followed by a series of heating-to-evaporation/recrystallisation stages, the aim of which was to extract the water-soluble aluminium sulphate and then concentrate the salt by boiling while at the same time removing solids and other water soluble impurities. For example iron impurity was removed as a yellow iron silicate crust known as 'slam'. Once a clear aluminium sulphate liquor was obtained then alkali (K^+) required for K-alum was added as a chemical. Another cooling/recrystallisation sequence followed to obtain K-alum crystals which are transparent to white.

What the 17–18th century practices clearly suggested was that the use of evaporation and fractional crystallisation with the aid of a continuous low temperature heat source like the geothermal energy available at the hot 'soils' of the small solfatara fields, like that of Aghia Kyriaki, Melos (Photos-Jones et al. 1999) could be the means by which *alumen* could have been processed/purified in antiquity on the island. Ceramic bowls (*c*. 30 cm diameter) representing *lekanae*, the type of pottery found in abundance on site (Photos-Jones et al. 1999), were used to contain solutions of local tap water and Melian *alumen* made up in 1 litre plastic bottles. The highest temperature measured for the evaporating liquid was ~60°C. The experiments are detailed in Table 2 and illustrated in Figure 1.

The first experiment was aimed at assessing the rate of evaporation of seawater. On the solfatara

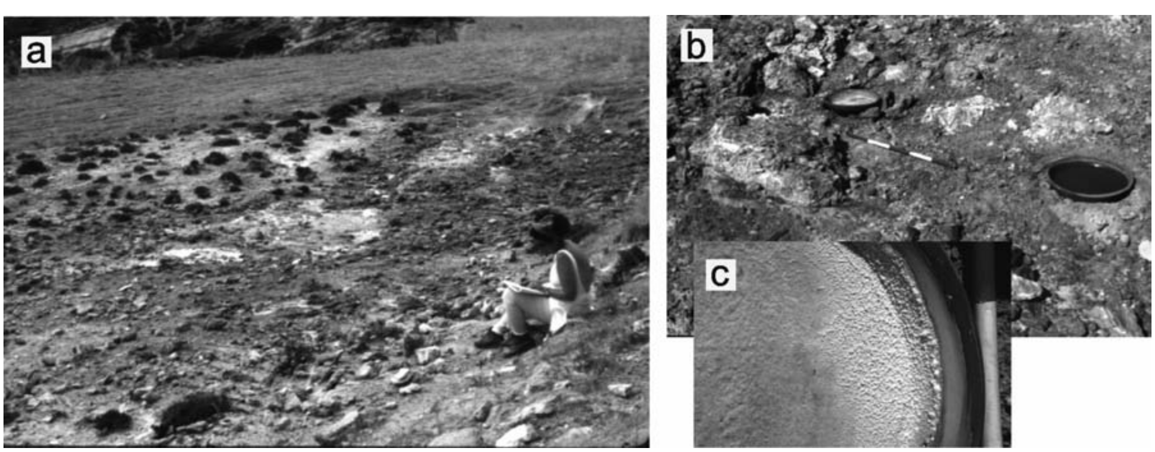

Figure 1: Experimental crystallisation in the field. a) solfatara at Aghia Kyriaki; b) 'lekane' on hot ground; c) salt precipitated from seawater.

Table 2: Processing of alumen: Field experiments

Procedure	**Result**	**Interpretation**
1 litre of seawater was placed in a ceramic pot on the hot ground of the solfatara; 1 litre of seawater (control) was placed on nearby normal ground (Fig. 1)	The seawater evaporated completely in ~4 hours; a white precipitate of sea salts formed (Fig. 1). The control lost only about 50% vol.	The hot ground has ample heat to evaporate solutions to dryness within a reasonable time.
~4 oz of a crushed friable alunite-rich Melian sample (XRD confirmed major quartz and alunite) was mixed with 1 litre of tap water and allowed to settle. 500 ml of solution was siphoned off to a ceramic pot. Left for 4 hours on hot ground.	The solution had evaporated to dryness leaving a trace of white precipitate.	There was a negligible content of soluble *alumen* in the original sample and alunite does not dissolve readily to provide *alumen*.
~4 oz of Melian *alumen*, an alunogen-rich efflorescence (confirmed by XRD) from Fyriplaka Cave (Hall and Photos-Jones 2005) was mixed in 1 litre of tap water. The sample dissolved leaving a few white granules. 500 ml of solution was siphoned off to a ceramic pot. Several pot sherds were placed on bottom of pot. Left for 6 hours on hot ground but sherds were retrieved after some precipitation.	Early precipitates on the sherds were confirmed by XRD and SEM-EDAX to be gypsum (Ca+S) and K-alum (S+Al+K+Al). A slightly yellowish crystalline crust formed over the surface (XRD confirmed major alunogen and SEM-EDAX confirmed major Al+S with minor K, Na and Cl in places). The underlying soft light grey paste contained some trapped solution.	After some precipitation of crystals the crystallisation process is more like freezing of water than evaporation of seawater. The surface deposit could have been scraped off and recovered.
A sample of efflorescent alunogen with some rock debris from Fyriplaka Cave was treated as in experiment 3.	Evaporation of 500 ml produced a gelatinous paste which was re-dissolved in a further 500 ml of water and left to evaporate again. A translucent material with the consistency of a thick syrup was produced.	Hydrated aluminous sulphates are rich in water and do not form distinct crystals within evaporating water.

evaporation was completed in *c.* 4 hours while on the surrounding soil evaporation took twice that time. The second experiment was aimed at establishing the solubility of an alunite-rich sample and its lack of solubility confirmed it could have provided either the 'solid' or the 'liquid' *alumen*. The third experiment was to assess the results of processing of an alunogen-rich sample. Evaporation resulted in the formation of a crystalline crust over a trapped solution, the process resembling freezing rather than evaporation. Experiment four was aimed to check the results of experiment three but with a different sample. The product was a gelatinous mass or paste presumably resulting from the incorporation of much water in the aluminium sulphate hydrate precipitate.

In summary, the field experiments demonstrated that the high heat flow at the solfatara at Aghia Kyriaki could have been used effectively to evaporate *alumen*-rich solutions and recover the *alumen* from 'mined' deposits that would inevitably have contained some insoluble rock debris. When solutions rich in alunogen are heated and allowed to evaporate a gel or paste can be produced. This is very intriguing and clearly points to Pliny's liquid *alumen*. The fact that K-alum is well known (Singer 1948) to crystallise as distinct transparent crystals could indicate that it represents Pliny's 'solid' *alumen*. K-alum is presumably more satisfactory than alunogen as a mordant, at least in part, because its purity is more assured by the crystallisation process involved in its formation

both in nature and industrially. Further experiments are therefore required to determine whether K-alum could have been recovered from the alunogen-rich deposits of Melos or whether a chemical process could have been used in Roman times to make K-alum from alunogen.

Impurities in alumen: laboratory tests for iron impurity

Singer (1948), in his review of alum and in consideration of Pliny's statement on pomegranate juice as a means of detecting impurities in *alumen* (*Nat. Hist*. 35, 184), suggested that the active ingredient in pomegranate juice must have been tannic acid. The term 'gallo-tannic acid' is used for compounds extracted from oak galls and other sources and used for tanning and dyeing; their chemical complexity and their role in dyeing is detailed in Cardon (2003). Therefore if iron (either ferrous or ferric) is present as an impurity within the *alumen*/alunogen then the gallo-tannic component of the pomegranate juice will react with the iron to produce a black solution of iron gallo-tannate. Iron sulphate has long been used in combination with sources of gallo-tannic acids, such as oak galls, to make black ink and ferric gallo-tannate has been confirmed to be a constituent of early black drawing inks by Burandt (1994) using XRF and FT-IR spectroscopy. The ink darkens after application as the original reduced ferrous form of iron, is oxidised to the ferric form.

In order to assess Pliny's statements on the use of pomegranate and oak gall juices (*Nat. Hist.* 34, 184–185) we have undertaken several experiments which are aimed to confirm that it is primarily iron sulphate in *alumen* that turns pomegranate juice black, and that pomegranate juice can detect even very small quantities of iron sulphate in *alumen*. Oak gall juice was also tested but tests were limited due to the difficulty in obtaining oak galls. As both pomegranates and oak galls contain gallo-tannic acids which are suspected to be the main ingredients in the reaction with iron impurity in *alumen*, and iron sulphate is the likely main form of the impurity in alumen, the reaction of iron sulphate with laboratory grade tannic and gallic acids was also examined.

Materials and Methods

The following pure commercial chemicals were used in the experiments: BDH ferrous sulphate (melanterite), $FeSO_4.7H_2O$; Aldrich Al-sulphate (alunogen) $Al_2(SO_4)_3.18H_2O$; Aldrich K,Al-sulphate (K-alum) $KAl(SO_4)_2.12H_2O$; Aldrich Mg-sulphate (Epsom Salts), $MgSO_4.7H_2O$; Aldrich ferric sulphate, $Fe_2(SO_4)_3.5H_2O$; Aldrich tannic acid ($C_{27}H_{24}O_{18}$); and gallic acid ($C_7H_6O_5$). Also used were: fresh Spanish and Greek pomegranates; a yellowish green and presumably young oak gall from an oak tree near Bothwell Castle, Uddingston, Scotland; and sulphate-rich deposits from Melos (Table 3). Deionised water was used for preparation of solutions and cleaning pipettes. All the commercial chemicals dissolved readily apart from a very small amount of the K-alum indicating that the solution was near saturated. Pomegranate juice was obtained by using a glass 'lemon' squeezer and filtering through a fine nylon mesh to avoid contact with metal. Melian samples used have previously been investigated using ICP-AES (Table 3) and powder XRDS (Hall et al. 2003a). Products in this study were investigated using powder XRDS and SEM-EDXA.

Results

The laboratory-based experiments (Table 4) established that pomegranate juice is a remarkably sensitive test for iron and can detect ~300 ppm iron in aluminium sulphate solution. The dark precipitate is almost certainly an iron gallo-tannate. The darkening

Table 3: ICP-AES analyses: soluble fraction. Concentration in original sample of water-soluble components (selected analyses from Hall et al. 2003a)

Sample soluble	%	Al ppm	Ca ppm	Na ppm	Mg ppm	K ppm	Fe ppm	Ti ppm	Mn ppm	S ppm	SO_4 wt% (calc)
AJH 5	86.2	74840	225	543	35	13611	226	21	3	157687	47.2
AJH 19	9.9	56	4203	12637	5501	777	12	1	7	10802	3.2
AJH 40	99.6	65852	2378	2584	835	26403	1996	22	319	125687	37.7
AJH 47	60.6	38701	478	2088	419	26331	1325	187	17	96827	29.0
AJH 54	94.1	80895	849	3313	293	358	1404	4	33	134559	40.3

Table 4: Impurities in alumen – laboratory tests for iron impurity

Procedure	Result	Interpretation
20 ml solutions for cations were prepared to 0.25 molar at room temperature using deionised water and the appropriate compound: Al^{3+} (Al-sulphate); Al^{3+},K^{+} (K,Al-sulphate); Mg^{2+} (Mg-sulphate); Fe^{2+} (ferrous sulphate); Fe^{3+} (ferric sulphate); and Al^{3+} (Melian *alumen* sample AJH40). 6 ml aliquots of each solution and a 'blank' of deionised water were placed in convenient plastic containers (30 mm square weighing trays) and arranged for comparison alongside corresponding trays containing 3 ml aliquots of each of these solutions mixed with 3 ml pomegranate juice.	The appearance of the original solutions (6 ml aliquots) was compared with the corresponding solution mixed with pomegranate juice. The appearance (before/after) of each of the samples were: Al^{3+} (colourless / dark red); Al^{3+},K^{+} (colourless / dark red); Mg^{2+} (colourless / clear red); Fe^{2+} (pale yellowish / black); Fe^{3+} (pale yellowish brown / black); and Al^{3+} (Melian *alumen*, slightly greyish / very dark brown.	Demonstrated that pomegranate juice produces a dark precipitate with both ferrous and ferric iron but not with K^{+}, Al^{3+} and Mg^{2+}. The darkening of Melian alunogen therefore indicates that some iron is present.
6 ml aliquots of 0.25 molar cations were prepared as for Expt.1. Also tannic acid solution was prepared to 0.125 molar. 0.5 ml tannic acid solution was added to duplicate aliquots of each cation solution.	The appearance of the original solutions compared with the corresponding solution mixed with tannic acid were: Al^{3+} (colourless / colourless); Al^{3+},K^{+} (colourless / colourless); Mg^{2+} (colourless / colourless); Fe^{2+} (pale yellowish / black); Fe^{3+} (pale yellowish brown / black with slight greenish tint); and Al^{3+} (Melian *alumen*, AJH40, slightly greyish / slightly greenish black).	Demonstrated that tannic acid reacts with the cations in the same way as pomegranate juice, confirming that tannic acid is the probable reactive ingredient in the pomegranate juice and iron gallotannate the likely dark precipitate.
10 ml of 0.1 molar ferrous iron solution was diluted by 50% in stages to produce aliquots of 2 ml each of systematically decreasing iron concentration. The eight aliquots contained: 0.1 molar (5600 ppm Fe); 0.05 molar (2800 ppm Fe); 0.025 molar (1400 ppm Fe); then 700, 350, 175, 88, and 44 ppm Fe. Each aliquot was mixed with 2 ml pomegranate juice.	The solutions darkened as the pomegranate juice was added to the iron-containing solutions. The darkening was much greater for concentrations of 700 ppm and above and was marked at 350 ppm (Figure 2a).	Demonstrated the sensitivity of pomegranate juice as a test for iron in solution. Concentrations as low as ~300 ppm iron can be detected.
Solutions of various Melian samples (AJH5, 40, 47 and 54) were prepared to ~0.1 molar (0.662 g in 10 ml). A 0.1 molar ferrous sulphate reference sample was also prepared. 2 ml aliquots were mixed with 2 ml of pomegranate juice and tannic acid to test for iron content.	The solutions of the Melian samples became dark on addition of the pomegranate juice and the tannic acid. The ferrous sulphate reference sample turned black on the addition of both pomegranate juice and tannic acid (Figure 2b).	Demonstrated that pomegranate juice (and tannic acid) produced a darkening of solutions of Melian samples, corresponding to their iron content expected from analyses of the soluble fraction of the samples.
Some liquid was extracted from an oak gall. Single drops were applied to a selection of powders, each on a watch glass, about 50:50 by volume.	The powders reacted as follows: Al^{3+} (no significant reaction, a slightly greenish yellow paste); Al^{3+},K^{+} (no significant reaction, a slightly greenish yellow paste); Fe^{2+} (black paste); Melian *alumen* (AJH40 – very dark green paste; AJH5 – yellowish paste, darkening with time).	Demonstrated that juice from oak galls is darkened by iron, presumably by the precipitation of iron gallate. Melian *alumen* (alunogen-rich) AJH5 appears to contain less iron than sample AJH40.
0.05 molar solutions of tannic acid, gallic acid, ferrous sulphate, K-alum and Al-sulphate were prepared and aliquots mixed as before.	Tannic acid, gallic acid and pomegranate juice all produced a black precipitate with ferrous sulphate but no reaction with K-alum and Al-sulphate.	The experiment confirms that gallic acid reacts in a similar way to tannic acid and pomegranate juice.

of the Melian solutions (Fig. 2b) correlates well with iron concentration but not well with manganese concentrations (Table 3).

Pliny's test could have been used by traders as a means of detecting low level impurities of iron. Oak gall juice could have been used in a similar way to pomegranate juice.

Impurities in alumen – laboratory crystallisation

Solutions of Melian alunogen (sample AJH40) were used to assess the possibility of concentrating *alumen* and removal of iron and other soluble salts using fractional crystallisation. The experiments detailed in Table 5 established that alunogen-rich samples formed a crust on evaporation of deep solutions (in a

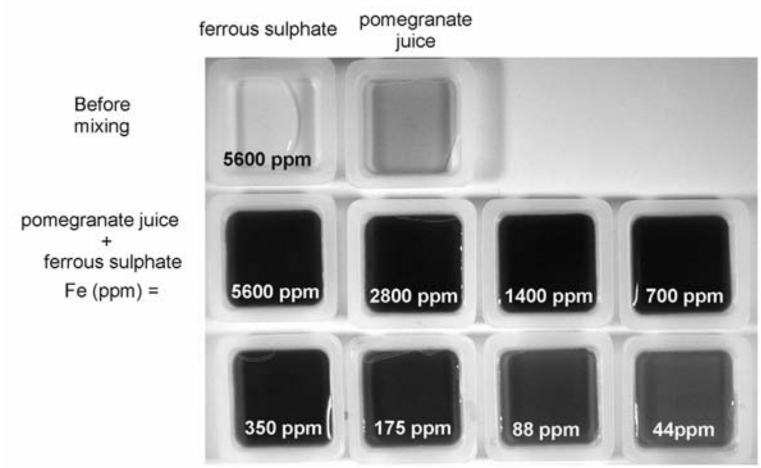

Figure 2a: Laboratory Experiment 3 (Table 4): Demonstration of sensitivity of pomegranate juice (reddish pink) in detecting iron. Correlation is more evident in colour.

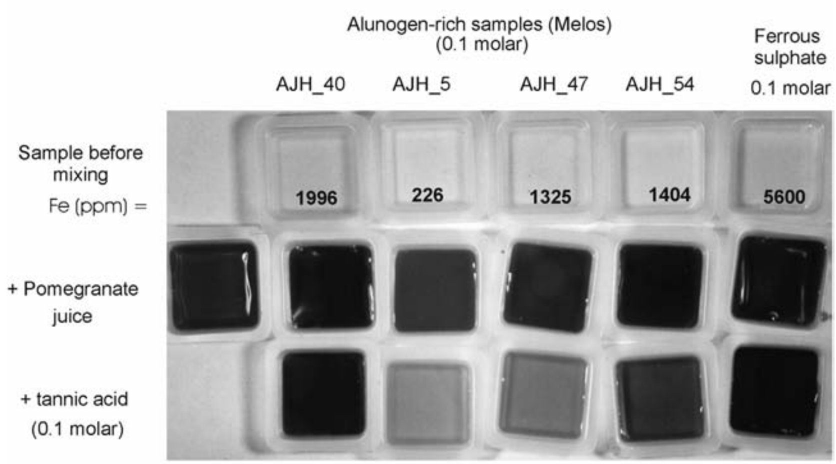

Figure 2b: Laboratory Experiment 4 (Table 4): Demonstration of sensitivity of pomegranate juice (purplish red, but appears almost black in the photograph) and tannic acid (pale yellow) in detecting iron in solution. The good correlation with iron content is more obvious in colour. Concentrations of iron as in Table 4.

beaker rather than a shallow watch-glass) and that there was no easily recognised (coloured) precipitate that was enriched in iron.

Impurities in alumen: Theoretical crystallisation

The field and laboratory experiments did not readily reveal a method of removing iron impurity but demonstrated that it was feasible that evaporation and fractional crystallisation could have been used in Roman times to recrystallise and purify Melian *alumen*. This process was considered further using theoretical computational aqueous geochemistry (Bethke 1996). A major advantage of this approach over experiments with real solutions is the ability to consider rapidly diverse chemical compositions and conditions.

'Experiments' were conducted to study the theoretical evaporation of *alumen* from Melos. Sample AJH40 which was known to be rich in Al-sulphate and relatively rich in impurities, including iron (Table 3) is presented as an example. Using GWB-REACT and the extended thermo.com.v8.r6+ database (Bethke 1996), 1 kg of water containing the dissolved sample (based on the analyses in Table 3) was 'evaporated' by progressive removal of 90% of the water. The program computes the theoretical solubilities of potential precipitates and calculates a saturation factor which increases as water is lost (Fig. 4a). Once the saturation factor for a particular phase, e.g. melanterite (Fe-sulphate), reaches its maximum solubility (factor = 0), the phase is 'precipitated' from solution and its chemical components removed. The

Table 5: Impurities in alumen*: Laboratory crystallisation.*

Procedure	Result	Interpretation
40 g of Melian *alumen* (AJH40) were dissolved in 50 ml of deionised water at 80°C and left for 1 hour to settle. After 15 minutes it was noted that the solution was turning slightly brownish. 40 ml of relatively clear solution was decanted into a 50 ml beaker and left to crystallise by evaporation in a drying cabinet at 40°C.	Crystallisation began around the edges of the surface of the solution and the crystalline crust spread over the solution preventing further evaporation. The crust was broken, liquid drained out into another beaker and evaporation continued. SEM-EDAX of the first crust to be precipitated confirmed traces of Fe, Mn and Ca in the host K,Al-sulphates (Figure 3) but slightly brownish precipitates did not show any significant enrichment in Fe and Mn.	There was no clearly defined early precipitation of iron-rich material.
A shallow concentrated solution of Melian *alumen* (AJH40) was evaporated on a watchglass. The white precipitate was sampled in three zones.	The first (outer) precipitate consisted of K-alum and alunogen. The next zone consisted of major alunogen and minor K-alum. The central final precipitate consisted of alunogen and very minor K-alum. SEM-EDAX confirmed these results but also demonstrated the presence of a K+S phase (probably arcanite) and some Ca-rich grains (probably gypsum) in the first (outer) precipitate.	There is no obvious precipitate that is enriched in iron (coloured).

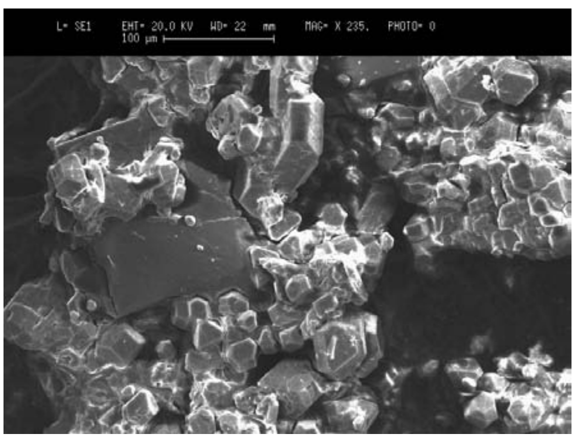

Figure 3: SEM photo of product from laboratory experiment 1 (Table 5) demonstrating that crystallisation of K-alum preceeds alunogen (confirmed using EDAX). Smaller crystals are K-alum (S>>K>Al, trace Ca) in setting of large cuboid crystals of alunogen (S>>Al). Some small gypsum crystals (Ca+S) occur in middle of field. Trace Fe and Mn present.

system is maintained at equilibrium in a series of steps as conditions change on removal of water. The change in chemistry of the solution can therefore be monitored and the mass of the phases precipitated can be determined (Fig. 4b). The calculations rely on the availability of appropriate thermodynamic data and unfortunately this is sparse for the diverse Al-sulphates. However, the calculations can be used to make predictions and to guide understanding.

During evaporation at 40°C (Figs. 4a and 4b), gypsum precipitates early but only a small amount. Most of the precipitate is K-alum and Al-sulphate (equivalent to alunogen). Iron sulphate (melanterite) precipitates after about 1/3 of the solution has evaporated but only a small amount of melanterite is produced because the initial iron content is relatively low. Significant evaporation is required in order to recover most of the Al-sulphate and by the time 90% of the solution has evaporated the precipitate has accumulated some Fe and Na impurities (melanterite, thenardite, halite). At a higher temperature, 80°C, which could well have been attained on hotter fumarole sites in Roman times, the Al-sulphate precipitates earlier and iron and other impurities remain in solution. So the extent to which precipitates of aluminium sulphate will incorporate iron impurity is a function of the temperature of the heat source, namely the solfatara; it is clear that this temperature could not have been controlled and may have varied from fumarole to fumarole. As such, even though the original 'batch' to be processed/purified may have been the same, if placed on different fumaroles a different degree of purification may have resulted.

Some iron could well be present in the ferric form in exploited *alumen* deposits and some would also be expected to form on oxidation of ferrous iron, albeit slowly, in crystallising *alumen* solutions; in this case the computation predicts that jarosite, the potassium iron sulphate hydrate, would be precipitated. It is noteworthy that in the geological process that leads to the origin of *alumen* deposits on Melos, iron (and manganese) is transported away from 'white rock' that is undergoing acid-sulphate alteration and is reprecipitated on oxidation as reddish brown ferric oxyhydroxides (Hall et al. 2003a; Hall and Photos-Jones 2005). The *alumen* deposits are therefore naturally low in iron.

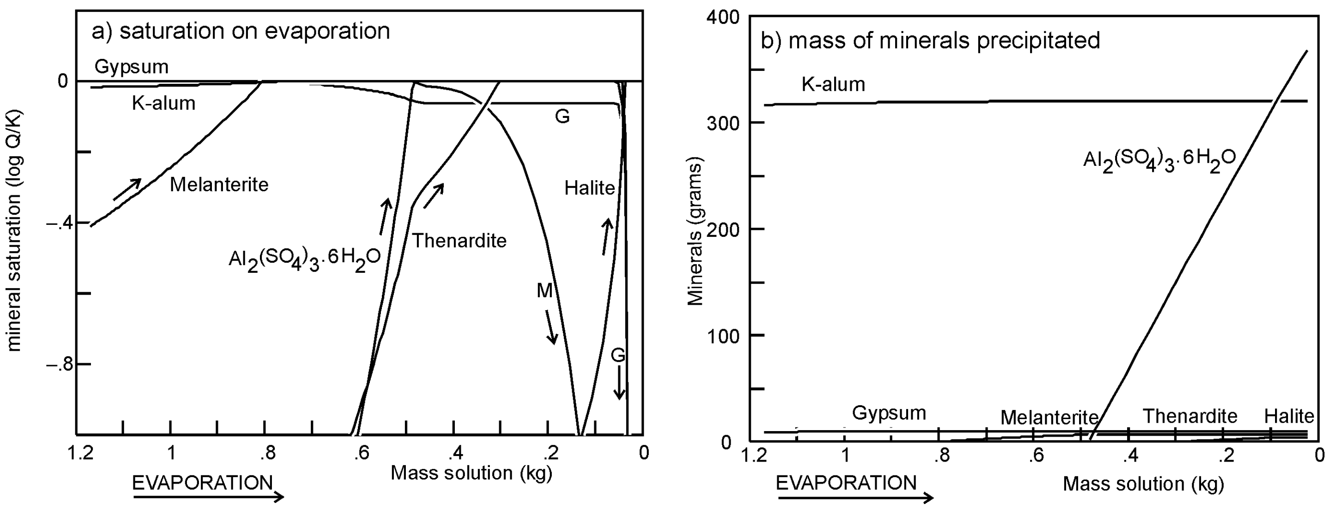

Figure 4: Demonstration of evaporation of impure alunogen-rich sample (AJH40) computed using Geochemist's Workbench REACT flow-through model (Bethke 1996). Nominal conditions used are: starting solution based on soluble fraction (see ICP analysis Table 2); temperature 40°C; 1 kg H_2O; 90% of water is evaporated. a) K-alum and gypsum (and anhydrite – removed for clarity) are saturated in the starting solution and precipitate immediately. The high iron impurity then leads to melanterite precipitation followed by Al-sulphate, thenardite and finally halite. KCl (sylvite) and Mg-minerals do not precipitate (arrows to aid interpretation). b) Weight of minerals precipitated. Note the substantial amounts of K-alum and Al-sulphate (taken to be alunogen) compared to others.

The computational evaporation 'experiments' indicate that a significant amount of iron would have stayed in solution if the temperatures were kept high (> *c.* 80°C) giving a lower iron content in aluminium sulphate precipitates. The residual hot iron-rich solutions would have presumably been discarded. Other scenarios for removal may have been possible, e.g. early precipitation of iron by addition of a reactive additive, or aeration to cause oxidation but these seem unlikely. Chemical and mineral wastes representing the undesirable components in *alumen* could feature in suspected Roman processing sites on Melos and the heavily iron-stained 'trough' located at site T6iv, Aghia Kyriaki (Photos-Jones et al. 1999) may be significant in this respect.

Discussion and Conclusions

The results reported above, based on geoarchaeological investigations, field- and laboratory-based experiments and theoretical computations, provide an insight into Pliny's comments regarding the 'liquid' (*phorimon)* and 'solid' *(paraphoron*) types of Melian *alumen* as well as the reagents (oak gall and pomegranate juice with tannins being their active ingredient) used to test impurities (iron sulphate) within both.

The geoarchaeological investigations clearly suggest that Melian *alumen*, either natural or purified, would have contained K-alum and K-free aluminium sulphates, such as alunogen. It is suggested that the significant impurity in *alumen* would have been iron although manganese warrants further consideration and possible investigation. Purification would have been achieved by partial crystallisation of solutions evaporated using geothermal energy (solfatara) as demonstrated in our field and laboratory experiments and using computational equilibrium thermodynamics. Experimental results suggest that if the source was rich in K-alum then the precipitate would have appeared as a solid, stemming from the fact that K-alum forms more distinct crystals, and would have been traded as *paraphoron;* if the source was rich in aluminium sulphates, e.g. alunogen, then the traded product could have been a gelatinous syrup or paste, in any case a more 'liquid' substance called *phorimon.* It is interesting that Pliny or later commentators of his (Levidis 1994) considered the *phorimon* the common and inexpensive variety. Aluminous sulphate, alunogen, is indeed more abundant and readily available on the island.

Phorimon was more likely to contain iron impurity in the form of iron sulphate than *paraphoron*. However theoretical calculations showed that the higher the temperature of the fumarole heat source, the higher the probability that most of the iron would have stayed in solution and would not precipitate out with the alunogen as *paraphoron* was being produced.

We can surmise from Pliny's statement that the pomegranate test was for *phorimon*, and the oak gall test was for *paraphoron*. However, it is not clear from our investigation why this should be the case; the use of one reagent or the other may have related to their seasonal and/or geographical availability or even simply to local practices. Either test could have been used either by producers or by consumers in antiquity and it was probably an accepted fact that whiteness of the material was not a guarantee for purity. Samples of Melian *alumen* (rich in aluminium sulphate) appear quite pure (white or off-white in colour) yet contain impurities such as Ca, Mg, K, Na, Cl and presumably most importantly, Fe. Significant concentrations of iron impurity would not have been detected visually. The detection limit of pomegranate juice could have been as low as ~300 ppm iron.

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Notes

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Chapter 19

Finding the Floorstone

P.T. Craddock and M.R. Cowell[1]

Abstract

From the Neanderthal mammoth-hunters of Lynford Quarry to the Napoleonic gun-flint knappers of Brandon, the unique qualities of the Floorstone beds of flint in the chalk outcropping in south west Norfolk have been much appreciated and sought. In the Late Neolithic this resulted in the sinking of the famous and extensive Grimes Graves flint mines. It used to be believed that the flint produced from all of the flint mines, including Grimes Graves, was primarily for axe production, but a major analytical project to provenance a large number of Neolithic polished flint axes to the mines failed to assign more than a tiny percentage to the Grimes Graves mines even though it was by far the largest mine and the Floorstone there has a very distinctive composition. Since our initial reports were published over 20 years ago, extensive field surveys in the East Anglican fens have uncovered very many flint scatters from the Mesolithic to the Bronze Age. The earlier material tends to have been made using secondary flint obtained from glacial tills or river gravels, but in the flint scatters of the Late Neolithic and Early Bronze Age black flint, sometimes still carrying the original cortex, is present, leading some to suggest that this was mined flint possibly from Grimes Graves. Analysis of a small sample of these flints confirmed that they were indeed of the Floorstone, and as Grimes Graves is the only significant working for it, strongly suggests that these pieces are the products of that mine. If that is so then it would seem that Grimes Graves flint was readily available in the Late Neolithic at least in East Anglia and a wide range of artefacts were made from it.

Introduction

We first met Mike Tite in the early 1970s, whilst he was still with the University of Essex, at Grimes Graves where he was collecting soil samples for soil magnetism measurements and we were engaged in soil phosphate analyses as part of a collaborative project to locate areas of human occupation at the site (Craddock et al. 1985; Hughes et al. forthcoming).

When Mike became the Keeper of the former British Museum Research Laboratory in 1975, a major project to provenance the flint used in the polished axes of the Neolithic back to their presumed flint mine source had already been in progress for many years (Sieveking et al. 1970, 1972). He encouraged us to bring the work to fruition and publication (Craddock et al. 1983). The original aim of the project to assign individual axes to specific mines was not successful. There were two main reasons for this which are examined in detail in the final fascicule of the report on the excavations carried out at Grimes Graves by the British Museum in the 1970s (Craddock et al. forthcoming), but which can be outlined here.

The initial assumption that the vast majority of the polished axes would have been made from mined flint is almost certainly erroneous; other secondary sources of flint were also extensively used, such as clay-with-flints deposits (Care 1979; Catt 1986; Gardiner 1984, 1987 & 1990; Barrett et al. 1991; Holgate 1988) and river gravels as well as small, temporary mines associated with specific major construction projects such as those at Durrington Walls (Booth and Stone 1952) and Hambledon Hill

Figure 1: Modification of the original Figure 2 from Craddock et al. (1983), showing the classification summary, with both the original pie-charts based on the complete set of analysed sites, with the addition of new pie-charts for the South Downs and East Anglia (to the right of the original charts), removing those sites now known not to be ancient. The effect is to increase the number of axes assigned to the South Downs and unassignables, and to almost totally remove the axes assigned to East Anglian sources (Anthony Simpson). In the Figure DU is Durrington Walls and ED is Easton Down (Wessex); CL is Clanfield, SDA is South Downs A group, made up of Long Down and Stoke Down, SDB is South Downs B group, made up of Blackpatch, Findon and Cissbury, and WH which is Windover Hill (South Downs); GM is Great Massingham and GG is Grimes Graves (East Anglia); BE is Beer Head, PE is Peppard and EH is East Horsley (Other).

(Mercer 1987). These sources were supplemented in East Anglia by flints contained in surface spreads of glacial till (Healy 1991 & 1998; Ashwin 1996; Brown 1996; Edmonds et al. 1999). In addition, Pitts (1996: 327–8) suggested that we had missed many Neolithic mines, but the more recent surveys of Barber et al. (1999) show that we had sampled most of the likely mines in southern Britain.

The other main problem was that it was not possible to give the flint from each mine a unique analytical 'fingerprint' that would allow the products to be unambiguously assigned to specific mines (although more recent work by Thomson et al. (1986) incorporating additional elements had some success in separating some of the South Downs mines). Thus, overall in the report on the project, we could do little more than state that it was likely that the majority of the flint axes from Southern Britain that we had selected for analysis were likely to have come from the South Downs mines (Fig. 1) but that about a third of the axes were unassignable to a mine. Given that the majority of the flint mines of the Early and Middle Neolithic are in the South Downs (Holgate 1991; Barber et al. 1999; Russell 2000) this was not an especially surprising conclusion.

Of the large number of flint mines that have been proposed at one time or another in East Anglia only Grimes Graves is proven (Barber et al. 1999: 74–80) and that is Late Neolithic in date, with radiocarbon dates in the third millennium BC (Ambers 1996 & forthcoming). At the time of our project it was believed that flint was also mined at Great Massingham, Norfolk, approximately 30 km to the north of Grimes Graves, and a series of genuine prehistoric flint artefacts and debitage from there were analysed. 14 of the 120 East Anglian axes we analysed were

Plate 1: Selection of flints from East Anglia sampled for analysis; 11 of the 15 were found to be of Grimes Graves flint. Note many still have their original cortex, suggesting they are of mined flint rather than cobbles that had previously been subjected to river and ice action before use. (A. Milton / British Museum)

assigned to Great Massingham. However, it is now believed that flint was never mined at the site, although surface concentrations of secondary flint may well have been exploited. The flint outcropping at surface at Great Massingham and other regions in central Norfolk equates geologically with the horizons mined in the South Downs and thus there is likely to be some uncertainty whether axes formally assigned to the South Downs mines by the statistical programme really do come from there or are from local surface deposits. The revised pie chart for East Anglia (Fig. 1) now shows a significant number of axes likely to be of flint from the South Downs mines and a large group of unassignables. The fact that more axes were assigned to Great Massingham than Grimes Graves in the original pie chart can be interpreted as showing that the surface flints, of which the Great Massingham material was typical, are likely to have been the main source for the axes rather than the putative and largely non-existent local mines in East Anglia. This hypothesis is given further credence by the compositional spread of the unassignables in which there are no obvious compositional clusters, suggesting that there are no major missing mines in East Anglia awaiting discovery.

Somewhat concealed in our 1983 report amongst the reams of otherwise negative data was a negative conclusion that was of rather more significance. This was that very few of the axes (two out of 400+ analysed) were assignable to the largest flint mine of them all, Grimes Graves. This was especially frustrating because it was the only mine where the mined flint did have an unambiguous signature, such that if Grimes Graves had been a major producer of flint intended for polished axes then we would have had no difficulty in picking them out. Thus in our 1983 publication we had to conclude with a question:

> 'Where are the axes? It is difficult to believe production on such a prodigious scale could have left so little evidence in the archaeological record. However, perhaps we have been looking for the wrong implement.'

This, however, was not to be the end of the matter, and both analytical and archaeological work continued.

Analytical work

Our work on the project was quiescent since the publication of the 1983 paper until recently, with the exception of a paper by Bush and Sieveking (1986). Some other analytical projects have been reported, such as that by Thompson et al. (1986) who investigated the application of the technique of inductively coupled plasma analysis to the analysis of flints from the mine sites, and claimed that the increased number

Table 1: Descriptions of the flints selected and concordance between their registration nos. etc. and the BM Laboratory sample numbers.

BM no	**Norwich no.**	**Description**	**Provenance**
GG 1	39.22 1.21 (18)	Scraper	Two Mile Bottom: Site XXI
GG 2	1932.124. A 2324	Polished Axe	Lound Run
GG 3	153.929 Box 1624	Fabricator	Methwold: Warburton site 2a
GG 4	A 1025 1.151 (in small box)	Flake	Methwold sites 1, 3 & 4
GG 5	32.926.28 A. 982 1926.32	Plane	Cranwich
GG 6	32.926.28 A. 982 1926.32	Flake	Cranwich
GG 7	32.926.28 A. 982 1926.32	Scraper	Cranwich
GG 8	15 3 929 A 979	Biface	Cranwich
GG 9	254 / 173 558 974 3	Flake	Cranwich
GG 10	16 8324 Box 984	Biface	Cranwich
GG 11	16.83 Box A978	Fabricator	Cranwich Site 76
GG 12	160. 938 Small box A	Scraper	Two Mile Bottom
GG 13	A 1029 153.929	Flake	Methwold
GG 14	39.22 A 1060	Polished biface	Thetford: St Peter's
GG 28	A998 544 969 TL74259145	Biface	Feltwell
BM no	Grimes Graves no		
GG 15	1914 8- 1 16	Axe	
GG 16	1973 475	Axe	Pit XII Floor D
GG 17	Balfour 1902	Axe	Brandon Park
GG 18	266 P. 96	Axe	
GG 19	74 238	Axe	950-820 F 24 (4)
GG 20	1914 8-1 86	Disc Knife	
GG 21	1924	Disc Knife	Pit 10 4′ 6′′
GG 22	(366)	Axe	Pit 10 floor 4
GG 23	GG 74 (233)	Axe	
GG 24	1914 8-1 32	Axe	
GG 25	GG 76 451	Axe	
GG 26	GG 75 Li 022	Axe	
GG 27	GG 75 LI 304	Axe	

of elements quantified (16) enabled them to uniquely characterise some of the mines that were previously inseparable, notably Cissbury from the other mines of the South Downs Group B (see below) on the basis of the barium and manganese content. The project did not progress as far as the re-analysis of any of the axe material.

Analytical work has also been reported on flint and related material from outside Britain using a variety of approaches. Matiskainen et al. (1989) used AAS to determine some 20 elements in order to differentiate the sources of the flint brought into Finland, principally from Denmark, but also from the flint mines in the western regions of Russia (Gurina 2000). With such a limited number of possible sources so far apart it is not surprising that the project was successful. Stockmans et al. (1981) reported the elemental analysis of flints from some Belgian mines and found only sodium to be of use as an indicator of source. Griffiths and Woodman (1987) applied electron spin resonance techniques to the provenancing of flints from Ireland, and Maniatis et al. (1989) applied the same technique to flint from north west Greece. Blet et al. (2000) have applied non-destructive laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) to the provenancing of flint from the south of France, thereby continuing the analytical studies begun with neutron activation analysis many years ago by Aspinall et al. (1976 & 1979). Consigny and Walter (1997) used particle induced X-ray emission to analyse flints and cherts from the Paris basin of the Ile-de-France and were able to differentiate stone from the same geological horizons but different geographic locations by their trace elements. Bressy (2003) provenanced Mesolithic and Neolithic flint artefacts from sources in the Northern Alps using a combination of petrology with inductively coupled plasma atomic emission spectrometry (ICP-AES) and ICP-MS. Shokler (2002), recognising the variability of flint composition, combined trace element analysis with other physical features of the flint such as colour, translucency and inclusions, in his provenancing study on flints from Portugal.

Others noted and speculated on this failure to recognise Grimes Graves flint away from the mines. Some pointed to the ritual aspects of the material and Ashwin (1996) seemed to suggest that the products were possibly being disseminated only well

Table 2: ICP-AES analyses of flints from field survey in East Anglia (1–14 & 28) (Plate 1) and of axes (Plate 4) and disc knives (Plate 5) from Grimes Graves (15–27).

	Artefact	Al	Ba	Ca	Fe	K	La	Li	Mg	Mn	Na	P
Norfolk Flint												
BMGG1	Scraper	529	15.7	671	57	301	1.4	4.14	24.6	2.1	265	157
BMGG2	Polished Axe	574	9.5	370	86	258	0.8	4.44	24.2	<0.1	303	97
BMGG3	Fabricator	582	1.8	307	76	227	0.9	16.73	17.0	0.1	209	68
BMGG4	Flake	671	2.1	645	75	283	1.6	5.38	21.7	<0.1	285	139
BMGG5	Plane	519	3.4	202	54	268	0.7	4.30	17.5	0.9	268	25
BMGG6	Flake	524	2.7	321	96	248	0.8	4.52	19.5	0.1	238	67
BMGG7	Scraper	598	5.9	433	69	267	0.7	4.85	18.6	<0.1	286	131
BMGG8	Biface	812	6.5	496	57	413	0.9	7.89	24.4	0.3	374	116
BMGG9	Flake	519	8.2	272	63	241	0.8	4.48	17.0	0.1	260	91
BMGG10	Biface	388	7.8	2032	67	201	1.1	12.99	25.5	1.2	197	54
BMGG11	Fabricator	663	9.5	339	68	320	1.2	5.68	17.9	<0.1	305	83
BMGG12	Scraper	629	4.2	314	105	316	0.7	5.50	23.0	<0.1	291	97
BMGG13	Flake	701	4.6	533	69	319	1.0	7.65	18.8	0.2	338	160
BMGG14	Polished biface	637	11.4	234	58	290	0.9	5.87	18.3	0.9	296	61
BMGG28	Biface	488	3.2	342	78	227	0.8	4.18	19.7	<0.1	241	81
	mean	**589**	**6.4**	**501**	**72**	**279**	**1.0**	**6.6**	**21**	**0.4**	**277**	**95**
	s.d	*99*	*3.8*	*431*	*14*	*50*	*0.2*	*3.5*	*3*	*0.6*	*44*	*38*
Grimes Graves Flint												
BMGG15	Axe	489	2.0	12229	255	232	2.0	6.65	101.6	6.9	266	285
BMGG16	Axe	391	2.3	2112	61	214	1.7	3.02	25.0	0.3	245	269
BMGG17	Axe	484	9.0	268	51	256	1.1	3.98	17.7	<0.1	274	84
BMGG18	Axe	555	2.3	476	61	234	1.0	4.74	17.0	0.2	278	111
BMGG19	Axe	423	2.6	839	84	201	1.2	3.12	20.7	<0.1	226	214
BMGG20	Disc Knife	485	2.5	375	59	196	0.9	4.30	15.4	<0.1	249	75
BMGG21	Disc Knife	425	2.1	356	57	190	0.8	3.55	14.9	<0.1	224	72
BMGG22	Axe	422	2.1	391	46	173	0.7	3.76	15.8	<0.1	216	95
BMGG23	Axe	696	3.8	431	64	301	1.1	6.23	19.2	<0.1	332	94
BMGG24	Axe	518	2.6	495	64	244	0.8	4.29	16.5	<0.1	296	108
BMGG25	Axe	489	2.0	434	55	220	0.9	4.18	15.9	<0.1	270	117
BMGG26	Axe	621	4.9	374	67	267	1.1	5.33	20.6	<0.1	310	82
BMGG27	Axe	552	9.0	2191	134	275	1.3	5.57	28.6	0.7	284	117
	mean	**504**	**3.6**	**1613**	**81**	**231**	**1.1**	**4.5**	**25**	**0.7**	**267**	**133**
	s.d.	*83*	*2.4*	*3128*	*55*	*36*	*0.4*	*1.1*	*22*	*1.8*	*33*	*71*

away from the region, a sort of Neolithic export-only policy. A number of important field survey projects were established in the 1980s and 1990s in East Anglia, including some concentrating on the fen edges lying between about 10 and 20 km west of Grimes Graves that produced enormous quantities of flints (Silvester 1991; Healy 1996). Some of the archaeologists involved in these survey programmes, notably Frances Healy in a prescient paper (1991) entitled 'The hunting of the floorstone', took up our question, in the more (literally!) down to earth context of the material being found on the field walking exercises, and suggested some of the material they had been collecting could be of mined flint,

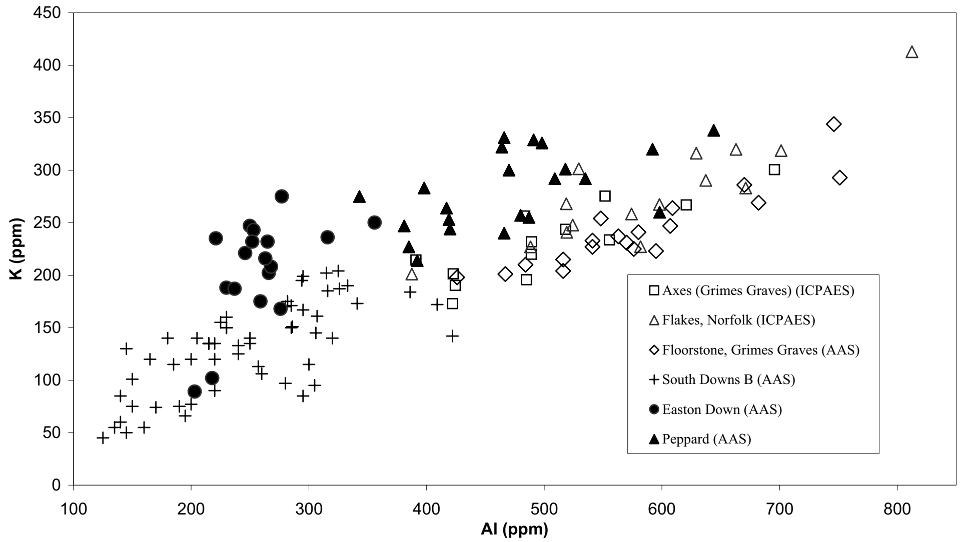

Figure 2: Comparison of the aluminium and potassium contents of the current samples of Grimes Graves and East Anglian flints with that of selected mine source data.

specifically from Grimes Graves. Analysis of a selection of this material (Plate 1) has shown that the majority is indeed of Floorstone, most likely to have come from Grimes Graves (Tables 1 & 2, Fig. 2).

At the same time as the large scale programmes of field survey were being conducted, John Lord, one time curator at Grimes Graves and amateur archaeologist, was carrying out systematic surveys of the extensive gravel quarrying operations taking place at Lynford, just a few km north of Grimes Graves. He found many flakes and artefacts that seemed to be of Middle and Late Palaeolithic origin (Plate 2), which led to the discovery of the extremely important Mousterian site where Neanderthals had been butchering mammoths (Boismier 2002). Lord noted that the artefactual flints had a different appearance from the majority of the gravels in which they were situated and, knowing of our analytical work on the Grimes Graves flint, requested our assistance to characterise the flint, as a result of which a selection from his surveys were analysed by us. They were found also to have the distinctive composition of the Floorstone and adjacent beds (Table 3), showing that the properties of this bed of flint were already appreciated in the Middle Palaeolithic, long before the mining of flint at Grimes Graves began.

The material

In the major programme of field survey carried out in the East Anglian fens through the 1980s and 1990s very many new sites were located, usually being identified by scatters of struck flint. Most of these

Plate 2: Typical Mousterian biface from Lynford Quarry. (John Lord)

pieces were made of flint that clearly derived from secondary sources, the glacial tills or river gravels. Their long surface exposure had caused much of the iron in the flint to oxidise, which together with the adsorption of iron salts from the soil has resulted in the familiar orange-brown colouration at least of the surface of the flint. It was noticeable that whereas the Mesolithic and Early and Middle Neolithic pieces all seemed to be made from flint from secondary sources, the Late Neolithic and Early Bronze Age material also included flints that were black and some still retained their original cortex. The cortex is the rather soft siliceous layer that formed the original boundary between the flint nodule and the chalk in which it had formed (Clayton 1986). It was reasonably argued that the cortex would have been lost if the flint had been exposed to glacial conditions in a till or

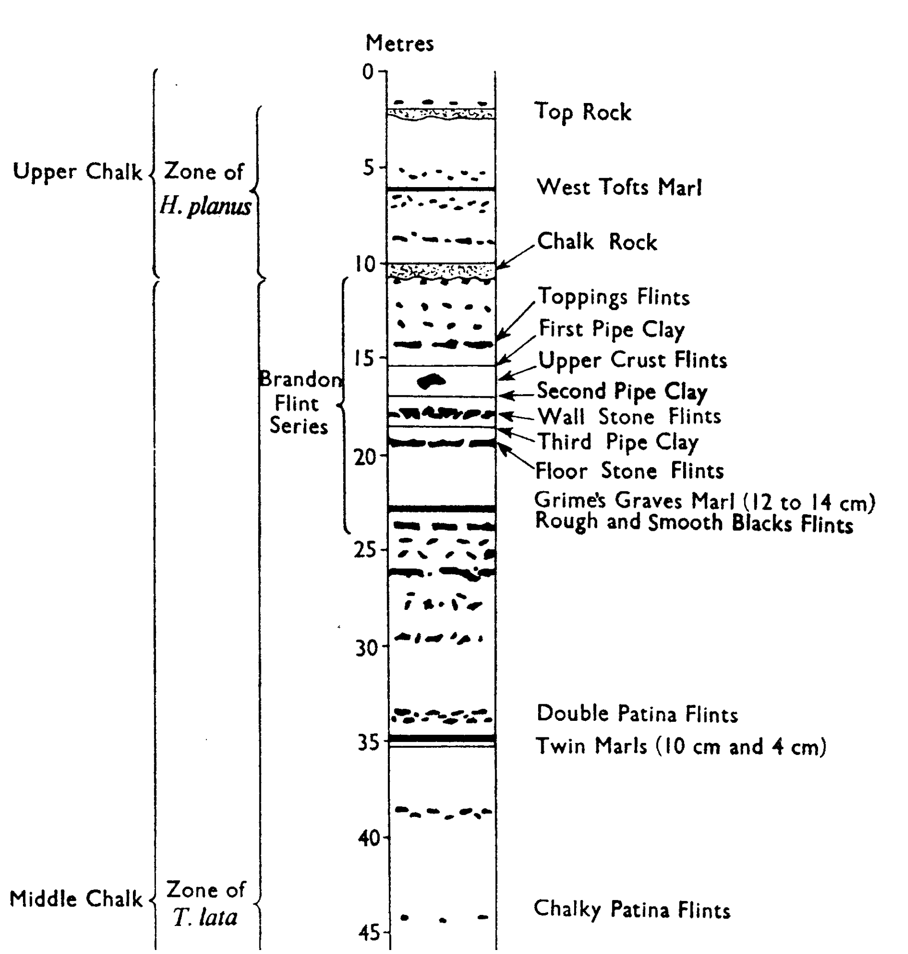

Figure 3: Schematic geological section of the Upper Chalk taken from boreholes at Mundford, near Grimes Graves, showing the stratigraphical relation of the various flint beds (from Ward et al. 1968).

in a forming gravel deposit. This suggested flints which retained their cortex had come from a primary source in the chalk, for which the mines at Grimes Graves seemed the most obvious location.

During the third millennium BC the formation of the fens began and many of the Late Neolithic and Early Bronze Age flint scatters are located on what would have been the margins of the forming peat bogs. Edmonds et al. (1999) and Healy (pers. comm.) suggested this peat formation would have covered many of the sources of secondary flint that had previously been available and as a consequence new sources had to be found. Presumably suitable nodules of flint occurring in exposures of the chalk would have been tried and the more or less continuous tabular flint layers of the Floorstone would have been noted and found to be flint with very superior working properties (see below).

The exact mechanisms by which the layers of flint formed within the chalk are still not certain, but it seems that they formed on the bed of the Cretaceous Sea, composed of silica derived from muds and sea creatures such as sponges (Mortimer and Wood 1986). Local changes in temperature, alkalinity and pressure caused the siliceous solutions to periodically precipitate forming the familiar beds of flint within the chalk as it built up (Fig. 3). The trace and minor elements found in flint are typically those of clay minerals, and the calcium content can fluctuate widely from parts per million to several percent in the space of a few cm across a single nodule. The other clay mineral elements are more stable. There are some local trace element variations within beds, but the main consistent variations are between the beds, that is geochronological variations rather than geographical (Cowell 1981a & b; Cowell et al. 1980;

Table 3: AAS Analyses of flints (Plate 2) collected by John Lord from the Lynford Gravel Pit.

No.	Al	K	Na	Mg	Ca
28572	640	254	299	16.6	370
28573	515	241	273	15.8	350
28574	660	271	308	18.6	345
28575	675	325	306	19.3	320
28576	645	281	288	23.4	970
28577	630	285	289	17.7	470
28578	535	245	253	16.5	510
28579	565	287	271	18.7	370
28580	590	233	274	18.0	635
28582	615	287	284	18.0	430
28583	675	327	308	20.9	435
28584	625	265	274	29.9	490
28585	730	290	290	20.1	430
mean	**623**	**276**	**286**	**19.5**	**471**
s.d.	60	29	17	3.7	172

Bush and Sieveking 1986). Put very broadly, the lower, earlier beds tend to have a greater trace element content than the higher beds, deposited towards the end of the Cretaceous period. In particular the aluminium and calcium contents seem to decrease, although the calcium content of the Grimes Graves flint is exceptionally low, which may contribute towards its unique properties (see below). The three main beds exposed in the sides of the Grimes Graves mines, namely the Toppings, the Upper Crust and the Floorstone, have similar compositions (Cowell et al. 1980, table 2). Originally the beds would have been deposited more or less horizontally but subsequent tectonic movement within the chalk has caused some change of angle; thus, in East Anglia the trend is for the chalk to dip from the West to the East. The effect of this is to limit the surface outcropping and near-surface occurrence of particular beds to within quite narrow confines, especially in relatively flat regions such as East Anglia. This results in marked changes in composition of the beds of flint occurring at or near surface across Norfolk, as demonstrated by the analyses given in Cowell et al. (1980, table 3). The secondary flints will tend to have come from the exposed upper levels, and the secondary flints from Great Massingham analysed as part of the original project provide a good exemplar of the composition to be expected. The trace element content is significantly lower than in the flints from Grimes Graves, but more similar to the flints mined from the South Downs etc. The average aluminium content is 318 ± 77, compared to Grimes Graves 530 ± 84 for example. This difference is of some importance, showing that the artefactual material we analysed from Lynford Quarry (Table 3) really is likely to have been made of deliberately selected Floorstone rather than from the secondary surface flint deposits which might randomly have contained a few Floorstone flints.

In many areas the upper beds including the Floorstone will have been lost through erosion; in others they will still be deep buried. The Floorstone seems to only occur near the surface in the south west of Norfolk, but here the chalk tends to be covered by large deposits of glacial sands and gravels such that exposures of the Floorstone flint are likely to have been confined to a few river banks etc. These could be sufficient for the needs of Neanderthal hunters perhaps, but if the flint was required in quantity then there was no option but to dig for it. In the Late Neolithic the properties of the Floorstone exposures in the dry valley now forming the north west edge of the mined area were discovered and over the course of a few centuries the Floorstone was followed into the chalk with the system of hundreds of interlinking shafts that are estimated to have produced 21,000 tons of flint (Longworth and Varndell 1996: 64). There are some putative early pits in the vicinity of Grimes Graves at Lynford and Buckenham Toft, Stanford (Barber et al. 1999: 74) that could also have been producing

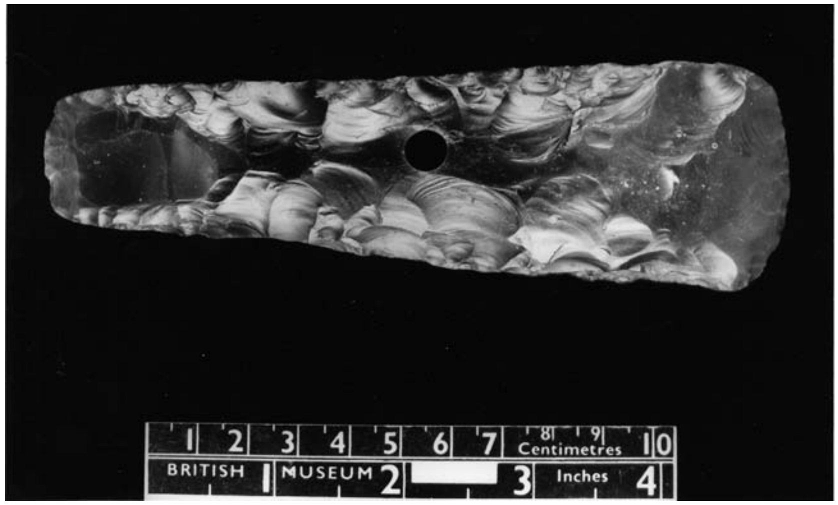

Plate 3: Polished axe from Lound Run, Belton, in Suffolk, also found to be of Grimes Graves flint. NB this was not part of the hoard of axes found at Lound Run which were not of Grimes Graves flint. (A. Milton / British Museum)

Floorstone, but even if they prove to be Neolithic, they are miniscule compared to Grimes Graves, which must be the source of the majority of the Floorstone produced.

The samples

For this project a selection was made from many field surveys and surface collections now held in the Castle Museum, Norwich. The selection was made by Frances Healy, Gillian Varndell and the authors. Fifteen pieces comprising a variety of artefacts or waste flakes were selected that had the appearance of being from a primary context, many retaining areas of cortex (Plate 1). One fine polished axe of black flint was also included because of its appearance (Plate 3). The only limiting factor is their size. Flint appears dense and impermeable but is in fact quite porous (Andersen 1982; Patterson and Sollberger 1979; Rottländer and Weymouth 1980/81). Thus there are potential problems of contamination during burial from groundwater containing the very elements necessary to fingerprint the source, and for this reason only larger pieces should be considered for analysis. In the previous project we had ascertained that the ground water had penetrated approximately two or three mm into the flint, and in order to be able to drill an uncontaminated sample core from the flint with a trepanning drill of about three or four mm diameter and about 10 mm in length the flint needed to have a minimum thickness of about 15 mm through a depth of about 20 mm. This precludes the meaningful analysis of small items such as arrowheads and thumbnail scrapers which have been previously suggested as products of Grimes Graves flint, and in practice only the larger core tools and large flakes were suitable for analysis.

Material was selected from Grimes Graves itself for comparison both with the flints from the surveys and with the analyses of the Grimes Graves flint from the previous project. One obvious reason for claiming that Grimes Graves was producing axes was that over 300 have been recovered from various excavations over the years. Thus a selection of 11 axes in various stages of production (Plate 4) were selected for analysis, together with two disc knives (Plate 5) which have also been suggested as products of the mine. As so few of the 120 axes from elsewhere in East Anglia had been assigned to Grimes Graves it was felt necessary to check that those found at the mine in such abundance really were of Grimes Graves mined flint. It is not completely improbable that the flint axes could have been brought to the site as, after all, two stone axes of Cornish origin have been found there (Clough and Green 1972: 133). It is believed that some of the axes were intended for use in the mining of the flint (see plate 3 in Longworth and Varndell 1996, for example), as has been suggested at some of the other mines in Europe (Weisgerber et al. eds 1980; Whittle 1996) such as those at Veaux-Malaucène, in the south of France (Schmid 1980; Weiner 2003) and Jublines in northern France (Bostyn and Lanchon 1998).

Plate 4: Selection of axes in various states of production from Grimes Graves. (A. Milton / British Museum)

Plate 5: Two disc knives from Grimes Graves. (A. Milton / British Museum)

Sampling and analysis

The previous analyses had been performed by a variety of techniques. In the early days of the project most elements were quantified by emission spectrography (ES), which was replaced by atomic absorption spectrometry (AAS) (Hughes et al. 1976; Craddock et al. 1983). The phosphorous was determined colorometrically. The previously unreported analyses of the material from the Lynford Quarry (Table 3) were performed in 1987 by AAS using the methods described in the 1983 paper.

For this latest project sample solutions were prepared in the same way as previously. The contaminated tops of the drilled cores were broken off with pliers and the cores then washed in nitric acid. After this they were digested with hydrofluoric acid to remove the silica, any organic material was oxidised with nitric acid and the residues were then dissolved in perchloric acid, following the procedures described in more detail in Craddock et al. (1983) and Craddock et al. (forthcoming), ready for analysis.

The sample solutions were analysed for 11 elements (Al, Ba, Ca, Fe, K, La, Li, Mg, Mn, Na and P) by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a Perkin-Elmer Optima 4300DV instrument. This is equipped for

either axial or radial plasma viewing. All elements were measured in axial mode which is generally more sensitive but typically has poorer precision than radial mode. In the previous studies eight elements (Al, Ca, Fe, K, Li, Mg, Na and P) were analysed, mostly by AAS. The three additional elements, Ba, La and Mn, are more sensitive by ICP-AES and were included to provide more variables with which to compare the two sets of samples. Matrix-matched multi-element standards were used for calibration and the samples were processed in two batches for high or low calcium as it was found that there was some interference from calcium at high concentrations, particularly on the sodium and potassium measurements.

Results

The current ICP-AES results are listed in Table 2. For comparison with other data, Table 4 shows the mean concentrations of the current results together with that of previous data for some of the relevant mine site groups, analysed by both AAS (Craddock et al. 1983) and ICP-AES (Thompson et al. 1986), and the floorstone flint layer from Pit 15 at Grimes Graves (Cowell et al. 1980). It can be seen from Table 2 that the majority of the flint artefacts from the East Anglian sites are very similar in composition to the Grimes Graves site artefacts for all the elements quantified. Furthermore, when they are compared with the other British mine site data in Table 4, they are clearly closest to Grimes Graves in composition. This is emphasised by a plot of the concentrations of aluminium and potassium (two of the main discriminating elements) for the current data with selected mine site data, South Downs Group A, Easton Down, Peppard and Grimes Graves floorstone (Cowell et al. 1980), in Figure 2. The plot shows almost complete coincidence of the two groups of the current data with that of the Floorstone from Grimes Graves whereas the other mine site data are almost completely separated from them.

A statistical analysis of the data has also been carried out. The methodology used was equivalent to that employed in the classification of flint axes by Leese (Craddock et al. 1983). All the flint mine data from the 1983 paper were included, with the current data for the Grimes Graves axes being added to the original Grimes Graves group. Different analytical techniques (ES and AAS as opposed to ICP-AES) were of course used in the original study; however, Thompson noted (Thompson et al. 1986) that there

Table 4: Comparison of flint artefact and mine group compositions showing mean values and, where available, the standard deviations for selected elements.

Flint Groups	Al	Ba	Ca	Fe	K	La	Li	Mg	Mn	Na	P
Grimes Graves and East Anglia											
Flakes, Norfolk sites	589±99	6.4	501	72	279±50	10.0	6.6	21	0.4	277±44	95
Axes Grimes Graves	504±83	3.6	1613	81	231±36	1.1	4.5	25	0.7	267±33	133
Floorstone Pit 15 Grimes Graves[1]	561±102	n.d.	727	50	246±30	n.d	5.6	20	n.d	267±39	98
Grimes Graves Flint Mine[2]	5510	2.6	420	62	210	n.d.	406.0	20	0.8	240	101
Grimes Graves Flint Mine[3]	663±115	n.d.	950	84	235±31	n.d.	6.0	25	n.d.	288±42	91
South Downs Mines											
South Downs A[3]	183±57	n.d.	3900	66	114±27	n.d.	5.0	34	n.d.	175±49	101
South Downs B[3]	247±71	n.d.	6750	87	130±43	n.d.	14.0	52	n.d.	159±63	81
Cissbury, flint mine[2]	240	<0.1	1620	64	142	n.d.	1.3	28	0.7	171	38
Blachpatch, flint mine[2]	270	6.4	7600	53	142	n.d.	7.8	56	3.5	141	59
Church Hill flint mine[2]	250	8.8	3150	44	128	n.d.	2.9	31	3.0	155	61
Other mines											
Peppard, flint mine[3]	472±76	n.d.	2900	104	280±37	n.d.	17.0	29	n.d.	287±61	98
Peppard, flint mine[2]	400	6.7	1680	71	210	n.d.	4.5	27	3.1	210	66
East Down, flint mine[3]	258±67	n.d.	7500	46	142±47	n.d.	13.0	55	n.d.	164±62	119
East Down, flint mine[2]	188	0.6	5900	26	110	n.d.	1.2	46	3.1	148	96

[1]AAS data (Cowell et al. 1980); [2] ICP-AES data (Thompson et al. 1986); [3] AAS data (Craddock et al. 1983)

Plate 6: This biface, perhaps the most competently knapped piece in the field survey selection, may not be of Grimes Graves Floorstone flint but possibly from a still deeper bed. (A. Milton / British Museum)

Plate 7: This axe found at Grimes Graves does not have a composition typical of Grimes Graves flint. (A. Milton / British Museum)

was no significant difference between his analyses of the mine site flints by ICP-AES and the original analyses by AAS. As in the 1983 study, the statistical method of quadratic discriminant analysis was applied with all data being log-transformed prior to analysis and using the same suite of elements (Al, Fe, Mg, K, Na, Li, and P). Initially, to test the separation of the groups, the control group items were re-classified using the 'jack-knife' method where each member is treated as an unknown. This gave a success rate for re-classification of 77% which is similar to that obtained in the 1983 study. The East Anglian flakes and tools were then classified using the 11 groups of mine data as controls.

Of the 15 items, 12 were classified to Grimes Graves, one (BMGG 3) was classified to Great

Massingham, one (BMGG 10) was classified to South Downs B (Cissbury etc.) and one (BMGG 5) was considered unclassifiable as it was assigned with almost equal probabilities to three mines (Grimes Graves, Great Massingham and South Downs B). Thus the majority appear to have been manufactured from flint derived from the Grimes Graves Floorstone. The three exceptions are almost certainly from secondary flint deposits within East Anglia.

BMGG 8, a large biface core tool (Plate 6), is rather interesting. Although it assigns to Grimes Graves, it has a significantly higher aluminium content than the Floorstone, suggesting the flint came from a bed geologically beneath. As the chalk rises to the west this flint could be from local gravels that were derived from one of the geologically lower beds that must have been exposed and eroded beneath what is now the fens, but the piece has the appearance of flint taken from a primary context and could be evidence for the occasional working of some of the geologically lower levels at Grimes Graves itself.

All but one of the Grimes Graves axes and both of the disc knives have compositions very similar to that of the Floorstone, strongly suggesting that they were of mined flint. The appearance of the one exception, BMGG 16 (Plate 7) suggests that it too was of mined flint, and it is probably no more than an analytical outlier.

The composition of the Palaeolithic material collected from the Lynford Quarry showed that it is of the Floorstone. There is, of course, no suggestion of reviving the old idea that the Grimes Graves mines could be Palaeolithic in origin (Smith 1912; Armstrong 1927). Grimes Graves lies at approximately 24 – 28 m OD, whereas the surface at the Lynford Quarry is at about 15 m OD. As the Floorstone and associated layers at Grimes Graves are at a depth of between six and 12 m depth, they would have been near surface at Lynford, exposed and washed out of the surface chalk by what was to become the river Wissey. It is also possible that the same exposures that attracted the Neolithic miners at Grimes Graves itself were also exposed much earlier.

Conclusion

After long years of being unable to find any body of material that assigned to the Grimes Graves Floorstone, it was very satisfying to find flints both from the Palaeolithic and Neolithic periods that did. Rarely, if ever, can a material have been so appreciated over such a long period of time as the beds of Floorstone occurring in the Brandon area of south west Norfolk. From the Neanderthal hunters of Lynford quarry, the Late Neolithic miners of Grimes Graves through to the more recent gun flint knappers, mining at Lingheath and Santon, near Brandon (Skertchley 1879; Forrest 1983) and Phil Harding of Time Team fame, using the Floorstone for his replication flint implements, the unique properties have been independently rediscovered through the millennia.

The selection of flint from primary contexts is already attested at the Lower Palaeolithic site of Boxgrove, in Sussex, where it is believed that flint for the hand axes etc. came from the chalk cliffs behind the beaches (Roberts 1986: 241). It is also attested at the early Mousterian site of Baker's Hole in Kent, where the appearance of the flint used for the large prepared core technique flakes suggested that it had come from a primary context, either from chalk cliffs bordering the Thames or possibly from then fairly recent solifluxion deposits (Smith 1911; Wymer 1968: 354–56).

What were the special properties of the Floorstone that were so deliberately sought through the ages? There is the practical argument that flint straight from the chalk will not have been subjected to frost action that can cause incipient cracks to develop in the flint. This in turn could cause tools such as polished axes to fail in use, probably only a short time after a considerable labour had been spent on their polishing (Harding 1987 took 26 to 30 hours to produce a polished flint axe). Suggestions of the ritual significance of mined flint also abound (Russell 2000: 119–21), the rational being that this was a material that had to be obtained with great labour, and not a little danger, from the dark bowels of the earth itself. However, even though mined flint in general may have had this prestige, it does not explain why the Floorstone was selected. Flint mines could have been sunk over much of East Anglia and flint successfully mined, but the only place where this actually happened was where the Floorstone beds outcropped. Furthermore, the Grimes Graves area was not an especially good place to sink mines as the chalk there is overlain by metres of loose sands. Clearly the Neolithic miners wanted the Floorstone for itself.

The flint in the Floorstone beds is relatively prolific, occurring either as continuous tabular flint or large nodules suitable for working. Also, by the common report of those making replica flint implements nowadays and of the 19th century flint knappers, the Floorstone flakes very easily and predictably. Those using the flintlock guns reported that the Brandon Floorstone flints produced a better spark and lasted longer than other flints. At that time it was believed that the quality of a flint could be judged by its colour and the 'Brandon Blacks' sold at a premium, such

that a minor industry of staining mottled flints developed (Skertchley 1879: 25). This could all be associated with the calcium content. As noted above, most flint contains thousands or tens of thousands of ppm of calcium, presumably in the form of calcium carbonate within the flint. This must necessarily interfere with the microcrystalline array of the silica, which in turn would render the flaking of the flint less predictable and otherwise tend to weaken it. Early man may well have appreciated the lustrous satin-black of the Floorstone flint aesthetically, but there were probably real practical reasons for doing so as well.

Most accounts of the activities at Grimes Graves assume that the mining of flint for axe production was the main purpose, as was very likely the case at the earlier South Downs mines (Barber et al. 1999; Holgate 1991: 38; Whittle 1996: 279–80), and the presence of axes and axe roughouts there is a powerful argument. Sieveking (1979: 39–40) and reported in Forrest (1983: 37–8), the director of the British Museum's excavations, although believing that axe production was not the only product of the Grimes Graves mines, still quoted figures of axe production variously of 20,000 or 30,000 per annum. However, the more detailed studies such as those carried out by Burton (1980) and Saville (1981) and latterly those of Lech and Longworth (2000, Figure 41) of the knapping floors etc. at Grimes Graves, with some exceptions (Richardson 1920, for example), generally concur that there is little direct evidence for axe production predominating. This change in attitude is reflected in past editions of the authorative site Guide books. Clarke (1963) assumed axe production 'was the purpose of the whole vast enterprise', but following the excavations of Mercer (1981) and the British Museum in the 1970s, Green in the 1993 Guide had to record that evidence for axe production was poorly represented on the chipping floors, before concluding that:

> More detailed studies are needed of groups of implements from Grimes Graves, and of flint axes and other tools in museum collections before any real conclusions can be drawn about the products made from the flint extracted with such labour over such a long period.

Our recent analytical studies have at last succeeded in recognising the Grimes Graves flint away from the site. The fact that large working flakes were discarded and sizeable core tools were not reworked suggests that Grimes Graves flint was readily available, at least in East Anglia. The overall impression gained, on an admittedly small and typologically skewed sample, is that Grimes Graves flint was in general use for a wide range of everyday tools in the Late Neolithic.

This project has not explored Late Neolithic flint scatters from further afield, although the comments of Edmonds et al. (1999) suggest that the same distinctive flints are also found in the Cambridgeshire fens. The true extent of the spread of Grimes Graves flint remains to be recorded but the analytical means to do so are now established.

Thus twenty years after what we thought was our last word on the subject, we have begun to find artefacts made from the Floorstone many millennia before its superior properties first attracted the attention of the makers of gun flints (Skertchley 1879; Forrest 1983). More specifically we have identified some of the products of the Grimes Graves mine and can at last report what was being made with the flint rather than what wasn't!

Note

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Chapter 20

'Sweet waste': The industrial waste from the medieval sugar refinery at the Tawahin es-Sukkar in Jordan

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Abstract

This paper looks at the contribution that materials analysis can make to the understanding of how early sugar refining was carried out in the Middle East in the post-Crusader period. The systematic excavation of a section of a waste heap at the sugar mill of Tawahin es-Sukkar, situated on the southern shore of the Dead Sea in Jordan, and thought to be one of similar Mamluk period (12th–15th centuries) establishments in the Jordan Valley, provided a wide range of materials amenable to laboratory analysis. Although sugar compounds as such continue to be elusive, calcium-based materials such as calcite and gypsum were recovered; there is indirect yet significant evidence that they may have served as the raw material for the clarification of the sugar solution and subsequently in aiding sugar crystallisation. The source of calcite/gypsum was probably the nearby sediments in the minerals-rich region of the Lisan peninsula.

Introduction

To a world accustomed to sweeteners in the form of honey, grape syrup, figs, carob and dates, the arrival of crystalline sugar into the West in the late 11th century AD through the mediation of the Crusaders must have been something of a culinary sensation. As one of the plant species featuring in the Islamic agricultural revolution (Watson 1983), sugar cane was introduced into the Middle East from the 11th century, whereupon its cultivation and the technology involved in extracting cane sugar soon spread across many parts of the Mediterranean. As Stern (1999) has put it, the late 12th century witnessed an *industrial revolution* (her italics), with sugar (production) clearly becoming an industrial export product. However, Horden and Purcell (2000: 258–61) see sugar cultivation as a demanding and costly process, irrigation being essential, just as extraction of the sugar was a technologically demanding process; the latter required considerable fuel supplies, a water supply, a large built structure probably dedicated to sugar refining alone, as well as a labour force.

There is ample evidence both in European and Arab documentary sources during the period between the 11th and the 15th centuries regarding the Ayyubid/Mamluk rulers' policy of promoting sugar crop plantation in the Jordan Valley by undertaking major irrigation schemes (Hamarneh 1977–8; Khouri 1988; Stern 2001). On the archaeological front, knowledge of the early sugar industry derives from the excavation of sugar mills located notably in the Jordan Valley, Palestine (Stern 1999; Hamarneh 1977–78) and, for the later periods, Cyprus, where there are especially impressive remains (von Wartburg 2001). In both Palestine and Cyprus, there are common architectural features that include the milling equipment itself, namely large grinding stones operated by water power, water chutes, boiling installations and associated firing hearths, and, as regards the material finds, the diagnostic and most frequent pottery is in the form of the distinctive sugar pots and molasses jars (Figure 1a and 1b). Our recent excavations of a sugar mill close to the Dead Sea in Jordan, Tawahin es-Sukkar (TES) (Figure 2), have begun to reveal

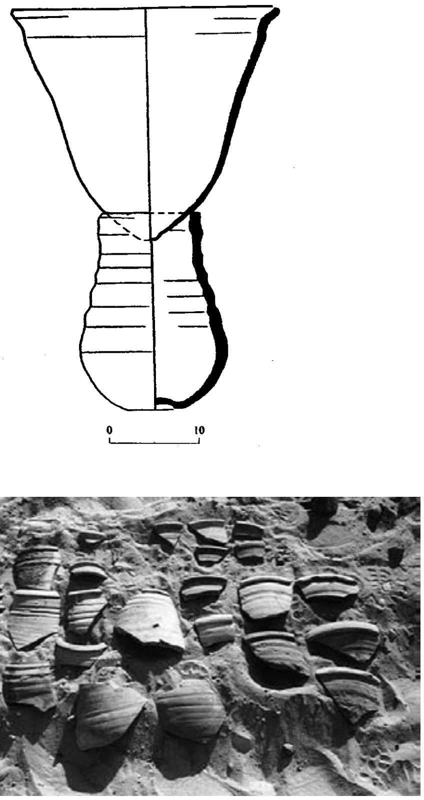

Figure 1: (a, top) Sugar pot and molasses pot of the Crusader period from the Hospitaller compound at Acre (Stern 2001: Fig. 19); (b, bottom) Fragments of sugar pots and molasses jars from Tawahin es-Sukkar.

similar good architectural and material remains (Photos-Jones et al. 2002; James 2002) (see Fig. 3).

Although documentary sources provide some background information about sugar, ironically for a foodstuff that is taken for granted in the modern world, there is apparently nothing visible today either of the end products of the refinery or any of the intermediate steps in the milling process. At TES the excavation of the mill room with its associated millstone proved to be devoid of organic remains (Photos-Jones et al. 2002). The analysis of residues found on sugar pots – the obvious first step in the investigation of the material remains directly associated with the industry – proved equally elusive, as the results of our investigations show below. Emphasis therefore shifted to the remains of a waste heap visible to the north of the milling room (Fig. 4) and systematically excavated at the same time as the latter; the aim was to provide a stratigraphic basis for looking at the nature and composition of all the waste products of the industry, be they pottery, charcoal, ashes, and a variety of unidentified materials labelled for convenience as industrial waste (IW) which merited further investigation. IW could be related to both the construction/demolition phase of the site, as well as the day-to-day waste generated by the industry. This paper focuses on samples of the IW featuring in different contexts within the waste heap, some of which, we believe, might have a direct relevance to the refining process.

The following sections provide a background to TES, a general insight into the mechanism of sugar production from sugar cane, followed by the analytical data relating to the waste products.

Sugar: composition and production

Early chemical analyses of sugar cane refer to the cut sugar cane, *saccharum officinarum*, as being very variable in composition (Jones and Scard 1909):

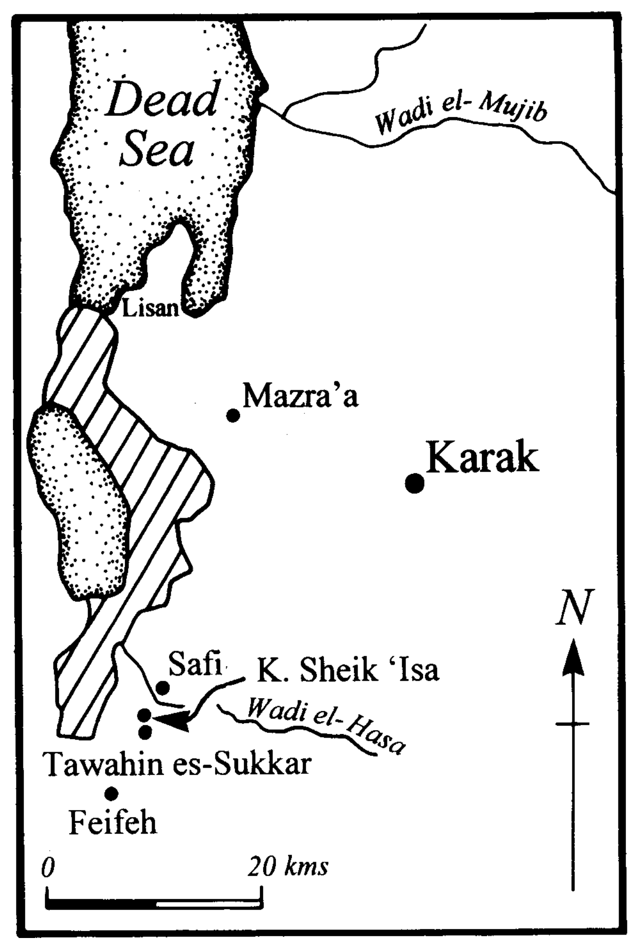

Figure 2: Location map showing Tawahin es-Sukkar and the Lisan peninsula to the north. The hatched area to the south of the Dead Sea has been drained.

Figure 3: View of the mill room from the north with the two chutes in the background. While only one chute would be necessary to operate the mill, the date and role of the second chute presently eludes us.

Water	69–75%
Sucrose	8–16%
Uncrystallisable sugar	trace–2%
Fibre	8–16%
Ash	0.3–0.8%
Organic matter other than sugar	0.5–1%

The main steps in sugar cane processing consist of: (a) crushing the sugar cane to extract the juice, a process originally carried out separately as pulp formation and subsequent pressing, (b) boiling of the juice to evaporate the water and produce syrup, (c) removal of both colour and non-sucrose substances using various reagents, and (d) sugar crystallisation from the melt and draining of excess liquor. It seems clear that an understanding of how to carry out and control steps (c) and (d) must have been in place before sugar manufacture would be possible, let alone expand on an industrial scale. At TES while the milling installations clearly point to a large-scale operation, the cane juice processing installations still lie under a considerable depth of sand and therefore cannot be gauged at this time. In the absence of any knowledge about the state of extant installations, attention has shifted towards scrutinising the sugar manufacturing waste.

Regarding sugar refining, a number of observations can be made. Since fresh cane juice is slightly acidic, all methods of clarification would involve heating with the use of an alkali, such as potash or lime (CaO) in order to prevent further acidification that would generate fermentation (Jones and Scard 1909: 126). We use the term 'clarifier' in a general way to incorporate a number of functions that include acid neutralisation and the removal of colour and unwanted impurities. At TES, these various reactions may not have been performed by a single reagent. Potash is known to have been used as the main clarifying agent, obtained by boiling ashes from a domestic fire; however, it was not as satisfactory as lime since it produced salts that interfered with sugar crystallisation (Jones and Scard 1909: 127). With larger scale production, and the use of the copper wall (a series of copper cauldrons) introduced in the 19th century, lime was employed. Alum and even herbs have also been listed as clarifiers as well as egg albumin (Clow and Clow 1952: 519).

Tawahin es-Sukkar

Tawahin es-Sukkar (TES) was surveyed by Frank (1934) who recognised it as an important manufacturing centre given the extant installations comprising of massively-built water channels leading to corresponding chutes. The date(s) of these installations are still a matter of investigation. TES has been included in a number of recent regional surveys (for example, Macdonald et al. (1992) and Politis (1998)), which established that the site may also encompass earlier (Byzantine) and later (Ottoman?) remains, be they pottery or buildings. Situated on a small hill with a commanding view to the Dead Sea, TES is well placed for a sugar mill: water from the nearby al-Hasa wadi is on hand; the sugar cane could have grown in the fields situated in the large alluvial fan spreading out to the north and west; and the minerals-rich Lisan peninsula lies a short distance to the north (Photos-Jones et al. 2002). Adjacent is the multi-period settlement site of Khirbat Shaykh Isa, originally a mound, about which MacDonald (2000: 57–8) states "there is little doubt that (it)….. was Byzantine-early Zoar(a)/Zughar or Sughar". This is no less than the fortified 'city' depicted on the Madaba floor mosaic of the 6th cent. AD, surrounded

by date palms and labelled in Greek 'Valak and/or Zoora'. The presence of sugar industry-related pottery at both sites suggests that perhaps in the 13th–14th centuries they were linked to each other as an industrial complex and its neighbouring settlement.

Topographic and geophysical surveys of TES and its immediate environs were able to clarify the overall layout of the industrial plan, as well as to reveal hot spots which were at the time attributed to hearths presumably from the boiling of cane juice (Jones et al. 2000). The 2002 short season of excavation (Photos-Jones et al. 2002; James 2002) made substantial progress in exposing the mill room, the water chutes (Fig. 3) and a lower vaulted room, as well as the main waste heap which was found to consist of a complex series of layers that are described below (Figs. 4 and 5).

The approach to the investigation of the waste heap

Recognising that direct material evidence of sugar would be scant or non-existent, the approach adopted was similar to that developed by two of us (EPJ, AJH) in relation to ancient industrial minerals exploited in the East Mediterranean, such as alum and sulphur (Photos-Jones et al. 1999). In both these cases the industrial waste from their processing was elusive in the archaeological record. In the present study this has involved searching for and identifying materials or compounds within the waste heap that might relate to the sugar production process. Systematic excavation (in 2002) of part of this waste heap at TES has been crucial in providing the relevant materials.

The stratigraphy of the waste heap was complex (Fig. 5), the most common waste material being what was termed at the time of excavation 'ash'. This pale-grey fine-grained powdery material found in layers may represent the remnants of fuel – most likely the dried crushed sugar cane after the juice had been collected – used in the heating of the sugar pots.

The second most common material (excluding pot sherds and natural materials) was an off-white material, both compacted in lumps of small or large size, but also in powdery form identified at the time of excavation as IW. Regarding the waste heap, there was a basal layer (context 217) consisting of sand and gravel with very dense vein-like patches running throughout and extending over the entire length of the trench. It was sealed by a relatively compact ash layer (216), a thin compact deposit of industrial waste (215) and another layer of sand and gravel (214). A dump of exclusively sugar-pot sherds (211) up to 0.35 m deep sealed these layers. Layer (211) was sealed in turn by industrial waste (213) that contained a thin lens of charcoal and 'ash' (218). The following layers alternated between thin layers of charcoal and 'ash' and thicker ones of sand and gravel and sugar-pot sherds (212, 210, 208 and 207). Layers of mud brick with varying amounts of pottery were then deposited up to depths of 0.4 m (209 & 206). On the surface of (206) was a large (0.3m x 0.25m) block of compact white material presumed to be industrial waste sealed by a layer of charcoal and ash (204). Compact 'ash'

Figure 4: View from the NE of the waste heap (Trench II) at the Tawahin es-Sukkar.

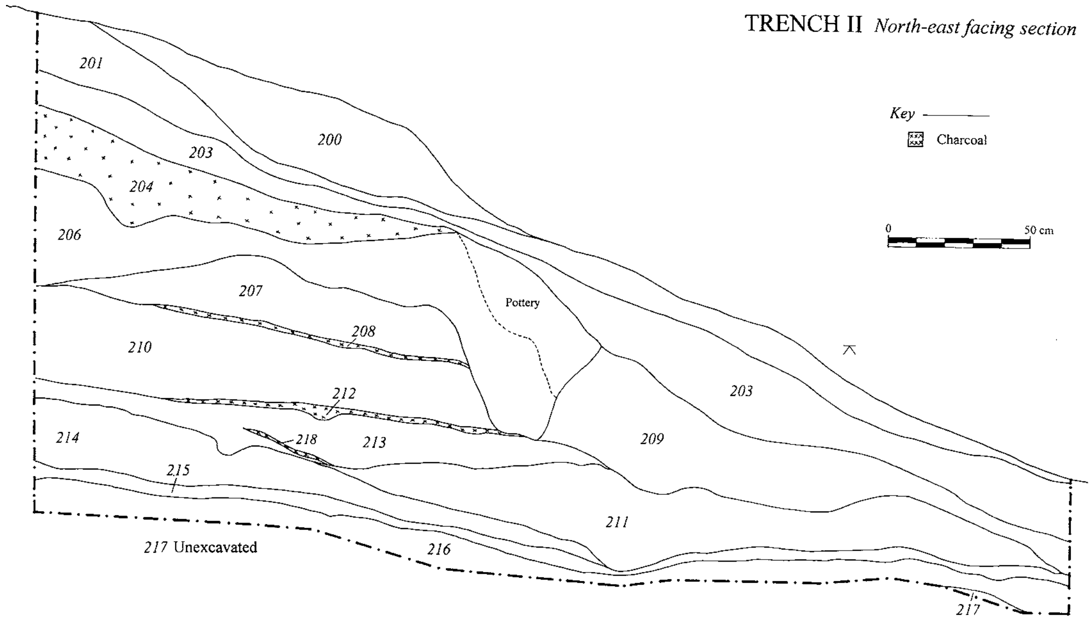

Figure 5: The NE facing section of the waste heap.

and a sand layer (203) overlay this, and the upper layers (201) and (200) consisted of loose topsoil and the spoil from a nearby robber trench respectively. As yet, the time span represented by the section of the waste heap is unknown, but it may reflect more than one phase of activities. In short, layers of sand and gravel alternate with layers of 'ash' and IW. The ash-rich contexts (such as 216 and 218) were distinct from the IW-rich contexts (such as 213 and 215), the former being ashy-grey, the latter off-white. Fragments of sugar pots and molasses jars, and perhaps vessels of other shapes, constitute another typologically distinct group.

Analytical methodology

The first task was to establish presence/absence of sugar in the accretions on the sugar pots. First examined with a binocular microscope, selected samples from the waste heap were subsequently characterised by powder X-ray diffraction (XRD) using a standard diffractometer with a Co-source, as well as a high intensity synchrotron source (at CCLRC Daresbury) (Salvadó et al. 2002), scanning electron microscopy with associated analyser (SEM-EDAX) and ICP-ES (for major, minor and trace element determinations). Whereas conventional XRD was performed on bulk samples, the particular advantage of the synchrotron source XRD was its ability to analyse very small individual particles found within a bulk sample; the possibility that some of these particles could have included sugar crystals was thereby checked. As regards organic analysis, this was limited to Fourier-transform infra-red spectrometry (FTIR) for the detection of sucrose and other components of sugar cane, such as di- and tri-carboxylic acids.

Results

Table 1 lists some of the materials from the waste heap and reference material from the Lisan. The first materials to be examined were the pale concretions or dark-reddish coloured stains occurring on some of the sugar pots from both stratified and unstratified contexts (Table 1). Analysis revealed that neither the concretions nor the stains had an organic component relating to sugar; the concretions were calcite-rich, the stains iron-rich.

The virtual absence of a detectable wax component in sugar cane negated the approach taken by Copley et al. (2001) in their chromatographic investigation of residues in 4th–7th cent. AD pottery from southern Egypt. From their identification in these residues of the fatty acids diagnostic of the date fruit wax, they inferred the preparation of a sugar-rich syrup from dates. In sugar cane, the organic matter, other than sugar, is less than 1%, of which only a very small amount (up to 5%) comprises wax esters to be found in the cane stem. Such a composition leaves little or no scope for the presence of any direct chemical marker of the raw material, sugar cane. As regards sugar itself, the situation is similarly

discouraging because of the speed with which it dissolves or decays. On the other hand, molasses has some potentially informative chemical indicators, for instance a relatively high mineral content; Chen and Chou (1993: 30f) quote 2.3–6.5% potassium, 1.1–3.4% sulphate, 12–19% sulphated ash and the presence of measurable quantities of some organic acids, in particular 2–3% of the tri-carboxylic acid, aconitic acid ($C_3H_3(COOH)_3$). However FTIR detected neither sugar nor these organic acids.

The second task was to characterise the nature of the off-white material identified as IW. Examination of specimens of IW from different contexts within the waste heap, whose descriptions are given in Table 1, revealed surprisingly uniform compositions; they were all rich in calcium (CaO 15–25%), low in aluminium (Al_2O_3<8%), iron (Fe_2O_3 < 3%) and alkalis (Na_2O and K_2O <2%); their Sr contents ranged from 189 to 598 ppm. The Lisan sediments were much purer calcium-rich materials (CaO > 35%) with very low minor element contents, but their distinguishing feature was their high Sr content: 1200–4100 ppm. These sediments and the waste samples differ as would be expected in their respective calcium contents, but significantly there is overlap in their respective CaO/Sr ratio ranges: 320–663 in fourteen samples of waste, and 170–507 in the Lisan sediments.

XRD results revealed calcite as the principal mineral; gypsum is found as the bulk material in only two samples, but it occurs in all other samples in sufficiently small amounts as to suggest it is a natural contaminant; there is variable charcoal/non-carbonised material reflected in the loss on ignition which ranges (in fourteen samples) from 10 to 25%, some or all of it deriving from the dried sugar cane used as fuel. One explanation of this contrast between appearance and composition may lie in the diagenetic processes of compaction, leaching and intermixing that have taken place in the waste heap during the lifetime of the waste heap and since.

We investigated the nature of the Lisan sediments as a means of establishing whether these deposits might have been the source of calcium in the calcium-rich IW. SEM images of Lisan sediments (132 in Table 1) show free acicular crystallites of aragonite (see Fig. 6), while those of grains of IW, consisting of quartz and calcite with minor dolomite, are plate-like and form clusters (Fig. 7a). Microscopic examination of 68 that had been dispersed (in the laboratory) in water indicated the presence of fragments not only of carbonised materials but also of fine non-carbonised crushed, ground-up organic remains resembling the cellular structure of sugar cane (Fig. 7b). We therefore infer that 68 contains both fresh and carbonised (ashed) sugar cane as well as abundant calcite. Regarding the aragonite, it was possibly lost in the process of lime production from the calcite-rich Lisan sediments. Crucial to the argument is the presence of high strontium in both Lisan sediments and IW; indeed IW (68) shows strontium sulphate crystals set in a matrix of calcite (Fig. 7c, d).

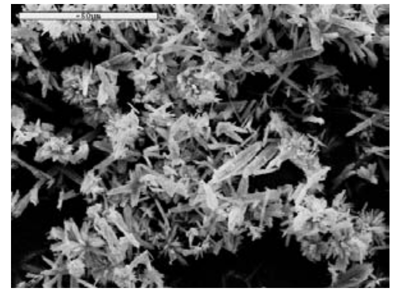

Figure 6: SEM-SE image of Lisan sediment (132) showing fine acicular aragonite.

Discussion

This short paper has drawn attention to the detailed excavation and sampling of a waste heap, followed by materials analysis as the means of shedding light on sugar production. Sugar, together with alum, belongs to that category of archaeological materials which although present is very elusive in the archaeological record. A methodology directed towards detecting such materials relies on associated rather than direct evidence and requires a good understanding of all components of the waste heap. At the time of the excavation at TES few contexts could be clearly characterised, and they were therefore sampled as industrial waste to be subjected to further examination. This revealed that most of the samples consisted of calcite or gypsum or both, calcite being the principal phase. The origin of this calcite can be traced to the Lisan sediments as testified by comparable CaO/Sr ratios and the presence of strontium sulphate in the industrial waste (Fig. 7c, d). Although the Lisan sediments are exceptionally fine-grained, a property which made them well suited to sugar refining, it is probable that natural recrystallisation processes have taken place during and after the use of the waste heap. An alternative or additional scenario would see the sediments being calcined to produce lime (CaO) which would convert rapidly back to the carbonate, the latter appearing on the dump as a hardened, caked slurry rather than as a powder. In any case, these scenaria have introduced a level of complexity which prevents at present a

Table 1: Descriptions of some materials from the waste heap at Tawahin es-Sukkar and sediments from the Lisan and a summary of their analyses (XRD (G) = bulk sample analysed at Glasgow; XRD (D) = very small selected sample analysed at Daresbury; U/S unstratified).

Sample No.	Context No.	Description	Analysis
Accretions on interior of sugar pots			
TES61	U/s	Pale, powdery encrustation	XRD (D): major calcite, quartz; minor kaolin, probable gypsum and possible aragonite
TES41	204	Granular white and black (charcoal) material coated with fine brown powder. Some fragments of pale brown crystals of gypsum	XRD (G): major gypsum, quartz, calcite; minor hydroxyapatite
43	206	Aggregate of soft white-pale brown, very fine-grained powder incorporating some soft cream acicular material (?gypsum)	XRD (G): major calcite, quartz; possible magnetite and haematite
TES62	U/s	Reddish stain, a thin crust on sherd many small (unidentified) peaks	XRD (D): major quartz, goethite, probable minor haematite; FTIR: Fe-O band; no organic phase
TES63.2	U/s	Dark stain, a thin crust on sherd	XRD (D): major calcite, quartz; minor kaolin; probable gypsum; two (small) unidentified peaks FTIR: carbonate band; no organic phase
Waste and ash			
68	212	Thin layers of charcoal and 'ash': dark fine-grained powder containing soft black grains, fibrous (charcoal); pale brown/cream powder /granules, white granules and very small transparent/translucent acicular crystals.	XRD (G): major quartz and calcite; minor dolomite; trace some possible kaolin.
61	213	Compact white/grey IW: compact grey/cream sample of fine-grained material with large voids. Has appearance of plaster. Surface dissolution evident.	XRD (D): major gypsum; trace quartz; possible trace site, gibbsite, celestite. LoI 7.2%. FTIR: no organic phases. ICP of bulk sample 25% CaO, 383 ppm Sr
62	U/s	Large cm-sized fragments of porous, compact and hard well-cemented material. Contains small pebbles. Large voids, some with white crystalline infill. Appearance of mortar.	XRD (G): major quartz; minor calcite and unidentified component; trace of possible gypsum. Unidentified peaks: probably a siliceous cement phase
66	208	Ashy charcoal and 'ash': subsample for XRD appeared as soft grey fibrous granules/ pellets with charcoal-like plant fragments	XRD (D): major calcite, quartz; minor gypsum, kaolin, possible aragonite; two small unidentified peaks FTIR: no organic phases LoI 21% ICP 15% CaO, 400 ppm Sr
46	213	Fine white powder contains fine-grained cream resembling plaster plaster	XRD (D): major calcite; trace quartz, kaolin, possible aragonite and possible gypsum fragments FTIR: no organic phases
72	215	Black powder with small grey pellets	XRD (D) of grey pellet: major quartz, calcite, kaolin; tr gypsum and possible additional traces. LoI 27% ICP 16% CaO, 349 ppm Sr
64	U/s	Composite of authigenic acicular crystals growing across gap, and material containing compact fine brown and grey lumps, and a white friable material with black and other inclusions.	XRD (D) of authigenic crystals: gypsum
Robber trench 10 m from waste heap, resembling the contents of context 215		Fine white powder	XRD (G): major gypsum, minor bassanite, anhydrite, aragonite, calcite and quartz
Lisan sediments			
125		Laminated white Lisan sediments from immediately south of Lisan peninsula	ICP: 44% CaO, 4200 ppm Sr
132		Lisan sediments from similar location to AJH 2	ICP: 37% CaO; 2900 ppm Sr
134		Gypsum in possible vein/infill in Lisan sediments, from similar location to AJH2 & 9	ICP: 38% CaO; 1200 ppm Sr

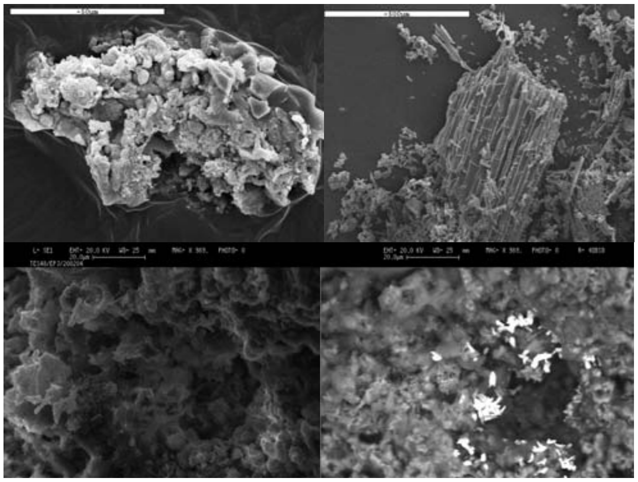

Figure 7: (a, top left) SEM-SE image of TES54 showing platy calcite aggregating as lumps; (b, top right) SEM-SE image of 68 following dispersion in water, indicating the presence of organic remains with a cellular structure resembling that expected of sugar cane; (c, bottom left) SEM-SE image of 68 showing platy calcite with small grains of strontium sulphate (observed to better effect in Figure 7d); (d, bottom right) SEM-BS image of the same area of 68 as in Figure 7c but displaying well the bright small grains of strontium sulphate embedded in the calcite matrix.

secure identification of the final stages of refining. But at least it can be said that calcite was the principal waste product from the clarification of the sugar solution: not only is it found on the interior of sugar pots, but it is also the dominant mineral within the heterogeneous materials within the waste heap. Gypsum may also have been used, but if so on a much smaller scale than calcite (and perhaps for another purpose?). Looking to the future, there is scope for more detailed analysis of the wastes: stable isotope analysis to confirm that Lisan sediments were indeed used in some way in sugar production, and chromatographic analysis to look for organic components present in low concentration.

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Notes

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